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BY George R. Jordan, USCO

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Division B

Section L-4

Report on Conversion of Nitrocellulose to Smokeless Powder (OD-22)

by George A. Richter

OSRD No. 72

Serial No. 9

January 17, 1941

Endorsement (2) from W. K. Lewis, Chairman, Section L-4, to J. B. Conant, Chairman, Division B. Forwarding report and noting:

"Because of the industrial importance of cellulose nitrates of low nitrogen content, a great deal of work has been done on them by commercial organizations. Because the high nitrogen products are so largely restricted to military use, they have not been studied to the same degree, or, if so, the information is kept secret. Were we under necessity of using wood cellulose for military powders, a comprehensive knowledge of their properties would be essential. Adequate information on the behavior of the nitrates with solvents might make possible the production of powders of quality and dependability hitherto unachieved. This basic information will never be secured except by Government effort, and probably only by a government organization. It is sure to have value for the Services and this value might well be of outstanding importance. In the light of our limited knowledge of these important fields, as disclosed by this report, I recommend the establishment under direction of Division B of a laboratory, correlated with that being organized at Bruceton and preferably located there, to give effect to the recommendations of the report and for the study of related problems."

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NATIONAL DEFENSE RESEARCH COMMITTEE

DIVISION B

Report on Conversion of Nitrocellulose to Smokeless
Powder

Serial No. 9

Copy No. 43

Date: January 17, 1941

Report No. 1 and 2 - Dr. Stewart
Report No. 3 - W. K. Lewis
Report No. 4 - G. A. Richter
Report No. 5, 6 and 7 - Dr. Stewart
Report No. 8 through 17 - Col. Adamson
Report No. 18 through 27 - Com. Hoover
Report No. 28 - J. B. Conant (Div. B file)
Report No. 29 through 40 - Div. B

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Serial No. 9

NATIONAL DEFENSE RESEARCH COMMITTEE

DIVISION B

Section L-4

"Report on the Conversion of Nitrocellulose to Smokeless Powder" (OD-22)

Endorsement (1) from Tenney L. Davis, Official Investigator and Member Section L-4 to W. K. Lewis, Chairman, Section L-4. Forwarding report and noting:

"Recommending consideration of the questionnaire."

(2) From W. K. Lewis, Chairman, Section L-4, to J. B. Conant, Chairman, Division B. Forwarding report and noting:

"Because of the industrial importance of cellulose nitrates of low nitrogen content, a great deal of work has been done on them by commercial organizations. Because the high nitrogen products are so largely restricted to military use, they have not been studied to the same degree, or, if so, the information is kept secret. Were we under necessity of using wood cellulose for military powders, a comprehensive knowledge of their properties would be essential. Adequate information on the behavior of the nitrates with solvents might make possible the production of powders of quality and dependability hitherto unachieved. This basic information will never be secured except by Government effort, and probably only by a Government organization. It is sure to have value for the Services and this value might well be of outstanding importance. In the light of our limited knowledge of these important fields, as disclosed by this report, I recommend the establishment under direction of Division B of a laboratory, correlated with that being organized at Bruceton and preferably located there, to give effect to the recommendations of the report and for the study of related problems."

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- 2 -

(3) Five copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee, as part II of two parts of Final Report, under contract with Massachusetts Institute of Technology, (Division B, #39). Division B, Serial No. 9.

"Special attention directed to recommendation of W. K. Lewis (endorsement 2). Comment and recommendations, on this part, of Army and Navy solicited."

J. B. Conant, Chairman

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CONVERSION OF NITROCELLULOSE

TO

SMOKELESS POWDER

Massachusetts Institute of Technology

Cambridge, Massachusetts

December 24, 1940

Prepared by
George A. Richter

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SUMMARY

1. The usual procedure by which cellulose nitrate is converted into smokeless powder grains is described in some detail.

2. Although serious reference is made to the behavior of the extruded grains during solvent removal, attention is directed principally to the colloidizing step preparatory to the extrusion of the colloided mass.

3. Literature search and interviews were concerned chiefly with items relating to:

- (a) A more uniform colloid.
- (b) Advantages that may result from a better choice of colloidizing agents.
- (c) The influence of cellulose nitrate viscosity in solvents on the behavior during extrusion and on the properties of the finished grains.
- (d) Volumetric shrinkage when solvent is removed from "green" powder.
- (e) Any peculiar behavior of wood cellulose nitrates as contrasted with cotton nitrates when colloided and converted into powder grains.

4. Most of the published investigations that bear on one or more of the above subjects have been made in laboratories outside of the United States and under conditions that are not directly applicable to present day schedules of the Army and the Navy. Much of the published work suggests important experimental programs with nitrate compositions and with plasticizer practice that are prevalent in this country.

5. Except for the introduction of FNH powders, very little advance has been made in the technology of colloiding the cellulose nitrates.

6. Polarized light and X-ray examination reveal that the powder grains as now produced are for the most part heterogeneous in composition. If a more homogeneous structure is beneficial, new methods must be sought to achieve this objective.

7. Although there is some difference of opinion regarding the relative importance of the nitrate viscosity on subsequent operations, it is generally conceded that present knowledge gives no serious evidence that low viscosity products are wholly unsuitable. The fact that the wood cellulose can be nitrated to yield products of high viscosity would seem to make the problem less important than it had originally appeared.

8. No data were found to follow the progressive changes in volume as "green" powder is freed of solvent. Some have expressed the thought that ununiformity of shrinkage (distortion of shape) was more of a problem than shrinkage of total volume. Total shrinkage is related to total solvent used in colloiding. Distortion of shape is related to manner in which the solvent leaves the grain.

9. It is the opinion of most of those who were interviewed that wood cellulose should offer no unusual problem in the

colloiding step if proper adjustment of solvent is made to compensate for a different plasticity of colloided mass. The powder grains of wood cellulose origin have been somewhat more brittle than in the case of the cotton products. Some believe that if needed this can be rectified by using a more refined wood fiber as a nitrating base.

10. This study has impressed the writer with the scarcity of direct knowledge relating to the subject and with the probable importance of unstudied phases of the problem. In view of this, a "questionnaire" has been prepared. It precedes the appendix and is submitted with the hope that it will stimulate further thought both in connection with current plant practice and in any new development work that is undertaken.

RECOMMENDATIONS

1. In a large degree the recommendations that were made in a preceding report entitled Wood Cellulose Nitrates for Munitions apply equally well here.
2. An advance will be made if a comprehensive experimental program results in:
 - (a) A more uniform product both in respect to keeping quality and ballistic properties.
 - (b) A more rapid colloidizing process.
 - (c) Less solvent cost.
 - (d) Greater capacity of extrusion presses.
 - (e) More efficient and more rapid solvent recovery.
 - (f) A completely satisfactory processing with wood cellulose nitrates.
3. It is recommended that the various items of the "questionnaire" undergo a critical review and that other pertinent questions be added. Those entries which in the judgment of the several reviewers appear most important may then be incorporated in the experimental investigations to follow.

INTRODUCTION

This report is primarily concerned with the colloidizing step by which nitrocellulose is prepared for extrusion into powder grains. Although there have been occasional instances of peculiar behavior of the cotton nitrates when so processed, this study was prompted largely because of new factors that were encountered when the wood nitrocelluloses are similarly handled.

The investigation has been in the form of a literature search and a series of interviews with men who have had considerable experience in the manufacture of smokeless powder and who have recently had the opportunity to witness the operations when carried out with a wood cellulose base. Men so interviewed included Dr. Hale and representatives of the Picatinny Arsenal, Dr. Farnum of Indianhead, as well as Dr. C. G. Storm of the Army Ordnance. The subject matter was also discussed with selected members from the technical staffs of the duPont Company, the Hercules Powder Company, the Eastman Kodak Company, and the Western Cartridge Company. Information relating to the principles that underlie the mechanism of cellulose ester swelling by means of solvents was also sought from certain faculty members of both Harvard and M.I.T. The author of this report has formulated a number of items which appear as a questionnaire which is intended to stimulate a more intense review and discussion. Some of the more important abstracts have been forwarded to Dr. Pauling together with a copy of the questionnaire that forms part of

this report.

Much of the information appears in fragmentary form and opinions regarding the principles involved are frequently a matter of conjecture. Reports are in some cases contradictory. The few facts appear incomplete and disjointed. Suggested lines of approach are indicated. Some of these proposed methods are little more than guesses; others may already have received some attention. If the problem has serious and practical importance to justify the work, it is evident that a comprehensive experimental program must be undertaken to establish the fundamental principles by which many of the experiences will be further explained and interpreted. Dr. Pauling has initiated such a program. It will prove helpful to supplement the laboratory investigation by an accumulation of additional data in the smokeless powder plant itself.

DESCRIPTION OF MANUFACTURING
PROCESS AND PRODUCT

The Colloiding Step

The purpose of the colloiding step is to create a condition that will enable the operator to convert the fibrous mass of nitrocellulose into a non-fibrous plastic which can then be worked into powder grains of specified dimensions and design. This is accomplished by pre-swelling the nitrocellulose with suitable solvents and by subjecting the solvent treated mass to a series of high pressure manipulations which ultimately take the form of an extrusion through dies of prescribed design. The preliminary mixing is done in a machine that resembles a dough mixer. Ordinarily about an equal weight of solvent is added to the nitrocellulose and the mixture is worked for a period of 20 to 60 minutes to assure complete wetting of the fibrous nitrate. The loose mass is then transferred from the mixer and formed into a solid cake by hydraulic pressure. Normally the product at this stage is a smooth compact colloid with a clear amber color. A few white spots are usually discernible and are caused by air bubbles. These are eliminated by further processing through a macaroni press in which the colloid is forced by pressure through small holes and the macaroni-like strings are again collected and reformed into what is known as the powder cake.

The powder cake is fed through the die press under 2000 to 3000 pounds per square inch pressure from which the material emerges as a continuous cord or cylinder having a

diameter and web such that when ultimately freed from solvent it takes on the specified dimensions of the powder grain that is being made. In the case of the layer grain powder the die is so constructed that the extruded continuous cylinder is perforated in a manner that is illustrated by the sketch which is attached.

Aside from the matter of chemical stability, solubility in selected solvents, and the like, a nitrocellulose is judged to be satisfactory for colloidizing and for conversion into powder grains when

- (1) its properties are such that the preliminary distribution of solvent is satisfactorily achieved;
- (2) the nitrocellulose is sufficiently uniform so that for a given grain size it is unnecessary to make frequent changes in the percentage of ether-alcohol used or in the die size;
- (3) the colloided block is clear and homogeneous;
- (4) extrusion takes place without breakage of deformation of the expelled strand;
- (5) the shrinkage of powder grains is uniform and predictable when solvent is removed;
- (6) the powder grains have a physical strength and toughness that withstands breakage when handled;
- (7) rate of burning of powder grains and the ballistic properties are normal.

Operating Procedure

Stabilized nitrocellulose is dehydrated By forcing alcohol

through the compacted nitrocellulose cake. Alcohol serves first as a means for displacing the water and finally as a dehydrating agent.

According to War Department Manual on Military Explosives, TM 9-2900, the amount of ether-alcohol solvent that is used for the colloidizing step is prescribed by the size of the powder that is to be made. Thus powder for a 30 caliber gun demands 105 per cent solvent, a powder that has a web thickness of .025 inch requires 100 per cent solvent, and a powder whose web is .135 inch calls for 85 per cent solvent. The different percentages, depending upon the size of grain, are very probably related to the shrinkage differences as caused by rate of solvent removed from the inner portions of the grain.

The residual alcohol in the press cake at the dehydrating press is controlled. The ether is added in the mixer in an amount which when blended with the residual alcohol that is in the dehydrated cake will yield a combined solvent that contains two parts of ether to one part of alcohol by volume. In some instances the alcohol content of the cake from the dehydration press is deliberately reduced and some alcohol is added to the ether that goes into the mixer. Prior to the addition of the ether, the nitrocellulose block is disintegrated in a block breaker in which the dense cake is pulled apart into small aggregates which are more suitable for the subsequent mixing operation. Time of mixing is specified at the shortest period consistent with good mixing and swelling of the individual nitrocellulose fibers. This will be discussed more fully.

The actual mixing with the solvent is accomplished in a two-armed mixer that resembles the machine that is ordinarily used in preparing soda cellulose in the viscose industry. The mixer is water cooled. At Indianhead the jacket water is reported to be from 55 to 65°F. The machine is tightly fitted to avoid solvent loss. One-half to one per cent of diphenyl amine is added with the ether. The amine functions as a stabilizer for the nitrocellulose. If plasticizers are to be used as in the case of the FNH powder, the dibutyl phthalate and the dinitro toluol are also added at this stage. The temperature of the mass during mixing probably averages near 60°F.

The mass as it leaves the mixer resembles a light brown sugar. By means of the heavy duty blocking presses and the macaroni presses, its plastic properties make it possible to produce a dense semi-transparent amber structure of hornlike consistency. If the mixing through the presses has been properly done and if the base nitrocellulose is normal in composition, the possibility of uncolloided nitrocellulose is practically eliminated. Dr. Storm reports that some work was done to improve the kneading operation by making use of machinery such as used in the rubber industry. These mixers have broad blades that force the material against the sides of the mixing trough under great pressure. Under such conditions more than mere mixing is accomplished. The resulting mixture loses its fibrous structure and can be processed directly through the final blocking press without passing through the preliminary blocking and "macaroni" presses.

Apparently the procedure was never put into general use.

Granulation of the powder is accomplished in the graining presses where the blocks of colloided nitrocellulose are forced through steel dies to yield a perforated heavy walled cylinder. The diameter of the strand is prescribed according to the size of the gun for which the ultimate powder is intended. The larger the bore, the greater the diameter of the strand. As the strand is carried from the machine, it is delivered over rolls to a cutting machine where it is reduced to units of desired length. In this form the produce is called "green" powder.

The green powder has lost more ether than alcohol. However, a considerable portion of the original solvent remains. Solvent removal is ordinarily practiced in two steps, a first recovery of the major portion by use of warm air from which the recovered solvent is later extracted by chilling, and an ultimate "drying" where solvent recovery appears impractical. It is very important to control the rate at which the solvent is removed in order to avoid a case hardening effect which makes it more difficult for the solvent to escape from the interior of the grain. The exact schedule of temperatures and time is carefully prescribed and is adjusted so that for the larger grains a longer time is allowed before the maximum temperature of 45°C. is reached. No reliable figures were obtained on the per cent recovery of the original solvent used. Indirect calculations indicate an 80 per cent recovery. A substantial shrinkage takes place as the solvent is removed. This shrinkage factor is very important and will be viewed

more specifically.

The final removal of solvent may be carried out by air drying or by water treatment. In the air drying procedure the powder is subjected to a preliminary temperature of 43°C. for 30 days, after which the temperature is raised to 55°C. and held there until the solvent contained has been reduced to the desired level. The time to accomplish this varies depending again upon the size of the grain. For small grain powders, 30 days may suffice. For large grain powders, 90 to 150 days are often necessary. In the case of the very large grains, it has been found advisable to hold the powder in the drying house for about two weeks before heat is applied. The drying is carried out until the grains have reached a specified solvent content which depends upon the size. For smaller grains the residual solvent may be as low as 3 per cent, for the larger grains as high as 7.5 per cent. This control is essential inasmuch as it influences the rate of burning of the finished powder.

In the water treatment that is sometimes used for the final removal of solvent, the powder grains are immersed in warm water by which the solvent is reduced to the desired degree. Time required is considerably less than in the air drying operation. Ultimate removal of water is also readily achieved. There appears to be some question regarding the successful application of the water drying step except when the NH (non-hydroscopic) powders are used. It is understood that most of the Army FNH powders are manufactured by the wet drying process and that the Navy pyro powder, which contains

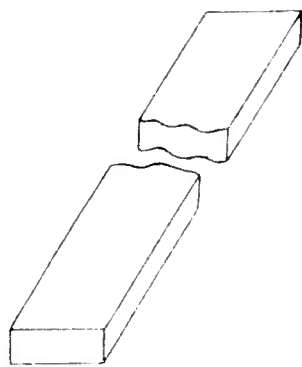
no dibutyl phthalate and dinitro toluol, is air dried. Whether the water drying step can exaggerate the difficulties of grain breakage when the nitrocellulose grain is near the lower level of acceptable strength is not clear although this information may be known to those who are close to the industry. There is also the possibility of some denitration except in those cases where the wet drying procedure is practiced with the FNH powders.

Powder Grains

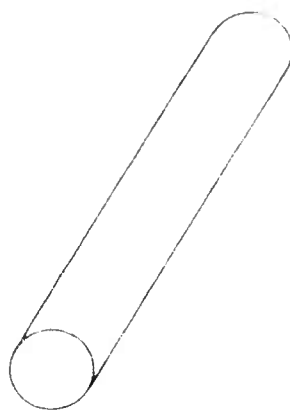
The War Department Technical Manual states that "the best form of granulation from a ballistic point of view is first, that which with the smallest weight of charge will impart to the projectile the prescribed muzzle viscosity within the permitted limit of maximum pressure; second, that which will cause minimum erosion to the bore; and third, that which shows maximum regularity in ballistics". The size and the design of the individual grain is a determining factor. The form determines the area of burning surface which in turn controls the rate of burning and ultimately the pressure.

The attached print shows several types of grain design. The strip, cord, and single perforated types are used mostly for smaller caliber guns. The rosette form is little used in this country. The multiperforated grain has received special attention in connection with the problem at hand.

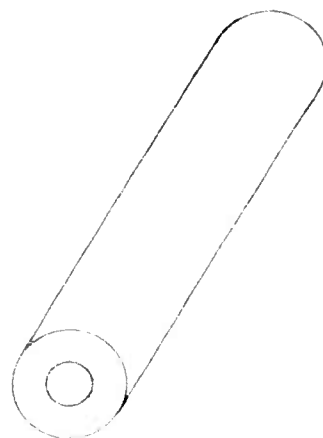
The print also shows the manner in which a multiperforated grain changes its form as burning takes place. When the walls have burned through, triangular pieces called slivers



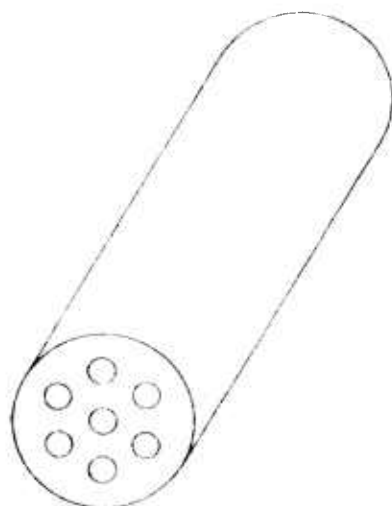
Strip



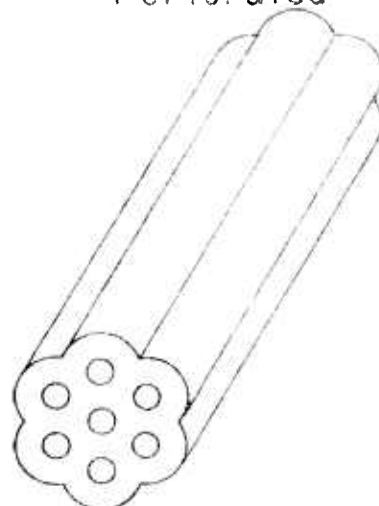
Cord



Single
Perforated

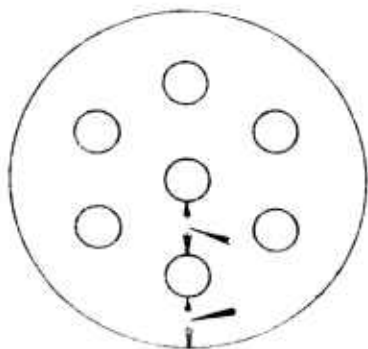


Multi
Perforated

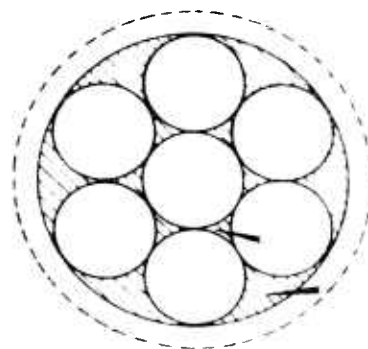


Rosette

FORMS OF POWDER GRAINS



Web



Slivers

CROSS SECTION OF MULTIPERFORATED POWDER GRAINS

remain and are frequently expelled from the bore of the gun in unburned form. The web of the grain is an all important dimension. It is the mean thickness between any two parallel surfaces. The "average web" is the mean between the outer and the inner webs. By varying the web thickness of the powder for a given weapon and projectile, it is possible to adjust the weight of the propellant charge to meet the ballistic requirements.

Length of grain is related to the grain diameter and to the diameter of the perforation. Thus in the case of multi-perforated grains the following formulae are used:

$$L = 2.25 D$$

$$D = 10 d$$

where

L = length

D = overall diameter

d = diameter of the perforation

It is ordinarily specified that the difference in the outer and the inner web thickness must not exceed 15 per cent.

With the single perforated grains the length is specified at from 3 to 6 times the overall diameter and the diameter of the perforation at one-third that of the grain itself.

Composition of Powder Grain

The single base powder grain contains:

(a) Nitrocellulose of prescribed nitrogen content. It may be a blend of lower and higher nitrogen content material as in the FNH powders or a single product as in the pyro powder that is produced by the Navy.

- (b) A small percentage of stabilizer.
- (c) A certain residue of solvent that was used in the colloidizing step.
- (d) A small residue of water.
- (e) Plasticizer if such is used in the mixture.
- (f) Graphite in the case of small arms (rifle powder).
- (g) Adventitious residues, (ash, etc.).

Tschappat point out that most of the ether has been removed from the grain in the drying process and that the solvent residue is largely alcohol. He also illustrates the importance of careful control of non nitrocellulose components inasmuch as they play an important role in the potential "energy" of the composite. Thus, he states, a one per cent alcohol content is equivalent to 2.5 per cent inert matter and that some stabilizers are equivalent to four times their weight as inert matter. He does not discuss the recently used plasticizers.

As already stated, the residual solvent in the powder grain is carefully controlled by frequent tests of the powder in its last stages of drying. The percentages specified depend on powder grain size and may range from 3 per cent in the smallest grains to as high as 7 per cent in the very large sizes. Special precautions are taken to avoid further loss of solvent. Conditions of storage of powder are very important.

Shrinkage of Powder During Removal of Solvent

The selection of die through which the green powder is extruded must obviously depend upon the shrinkage of the

grain during solvent removal. Although shrinkage takes place in all directions the one that is most important is that which occurs in the web. Shrinkage in length of grain may range from 5 to 10 per cent, whereas the web shrinkage is nearer 30 per cent, showing a distinct orientation of the cellulose nitrate chains in the process of extrusion. The inner web shrinkage in the case of multiperforated powder is generally less than the shrinkage of the outer web. It was reported at Indianhead that whereas the web shrinkage in the case of both the cotton and the wood cellulose nitrate powders was about the same, namely 28 per cent, the shrinkage along the length of the grain was about 3.4 per cent in the case of the cotton and 1.3 per cent in case of the wood cellulose products. It must be remembered that these data relate to a wood cellulose nitrate containing 12.6 per cent nitrogen and produced by the Hercules Powder Company. No corresponding figures were obtainable from the fabrication records of powder that was made by the FNH formula.

Although there is little documentary evidence, experience shows that shrinkage can vary widely with the amount of solvent used, the properties of the nitrocellulose, the size of the grain, and possibly with the type of solvent used. It is common practice to make the selection of the die after experimental lots of powder have been prepared from a given colloided mixture. Ununiformity in nitrocellulose or in processing may occasion frequent changes in die size to maintain a desired grain dimension. It is reported that in some instances the diameter of the green powder increases during a period after

it has been extruded and before evaporation of solvent takes place. This post swelling phenomena is mentioned again in the "questionnaire" and some general explanation is offered.

The Action of Solvents on Nitrocellulose

When solvents are added to nitrocellulose, swelling occurs and if enough solvent is present, the gelatinized mass then passes into a liquid solution. The path is not clearly defined. The rate and the degree of swelling depends, among other things, on

- (a) the composition of the nitrocellulose;
- (b) the physical properties of the nitrocellulose;
- (c) the solvent;
- (d) time, temperature and manner in which mixing is effected.

No explanation of the mechanism of the phenomena is here attempted. That phase of the problem is part of the study that has been undertaken by Dr. Pauling. This summary confines itself to a record of pertinent references in the literature, to the suggested explanations of the technologists who were interviewed, and to a number of viewpoints that have occurred to the writer.

Most evidence points to the fact that nitrocellulose as made commercially is not a "pure" product but a composite that contains components with different percentages of nitrogen. Two samples of nitrocellulose may contain identical percentages of nitrogen and show very different analysis when fractionated by means of selected solvents. It is well known

that the several nitrocelluloses respond very differently to the usual solvents. The high alcohol solubility of certain low nitrogen products and the alcohol insolubility of the 13.4 per cent product illustrate the point. Hence mass treatments of commercial nitrocelluloses of the same nitrogen content can show very different behavior. Weissenberger (U-7) gives some experimental data to show that cellulose nitrates as made commercially are composites of several nitrates, and in some cases with unnitrated cellulose remaining in the composite.

Kanamaru and Ueno (D-2) describe a new process for determining the swelling properties of cellulose esters. The work is confined to a nitrocellulose that has a 13.5 per cent nitrogen content. This nitrate was prepared by the authors. Nitrating acid contained 63 per cent sulfuric acid, 27.5 per cent nitric acid, 9.5 per cent water. The product was carefully purified and dried in vacuum and over P_2O_5 .

The following reagents were used either by themselves or in mixtures: ethyl alcohol, ethyl ether, benzol, acetone, ethyl acetate. Description of method and of units is given in great detail. The swelling properties are judged directly by the change in Z potential with time. Although the data includes a great many figures that deal with other solvent mixtures, attention is directed at this moment to the figures that relate to ether-alcohol compositions. The experimental program included work that was done with 100 per cent ether, with 100 per cent alcohol, and with various percentages of each. Although a detailed abstract is included in the appendix

of this report, it is well to note here that in a summary table the authors show that a maximum swelling effect is reached with a mixture that contains 40 per cent ether and 60 per cent alcohol by volume. The following figures are cited:

Ether-Alcohol		
Vol. % Ether	$\frac{\Delta Z}{Z_0}$	Q (degree of swelling)
0	6.63	9.2
20	79.43	36.5
40	87.46	73.1
60	84.42	57.5
80	45.17	26.0
100	4.00	2.8

$$\Delta Z = Z_0 - Z$$

where Z_0 is the potential immediately after immersion and Z_∞ is the asymptotic value of the potential reached after a number of hours.

Q = grams of solvent taken up by 100 grams of nitro-cellulose.

Note particularly that there is not a major difference in swelling properties in a range from 20 per cent ether to 60 per cent ether. The overall difference in that particular range is shown by the Z potential factor of 79.43 in the case of the lower ether mixture to a maximum of 87.46 with the solvent that contains 40 per cent ether and a reduction in the factor to 84.42 when the ether content of the solvent has been increased to 60 per cent.

Measurements were made to determine the degree of swelling and here also the maximum value was obtained with a solvent that contains 40 per cent ether. The difference in degree of swelling with lesser and greater ether contents in the solvent is more marked than is shown in the table of Z

potential factor.

In the J. Soc. Chem. Ind. of Japan, 1938, Kanamaru, Takada, and Maeda (C-11) discuss similar work that was carried out with pure solvents and with nitrates that contained respectively 13.52 per cent, 13.37 per cent, 12.83 per cent, and 12 per cent nitrogen. All of these nitrates were prepared by the authors. The swelling properties were studied in much the same manner as described in the article cited above. In this case emphasis is placed on differences in behavior of the nitrates with each of the solvents in question. The three solvents specifically studied were water, ethyl alcohol, and methyl alcohol. It appears that the methyl alcohol is a much better swelling agent than ethyl alcohol. This holds for each of the nitrates studied. It is interesting to note that in the case of the methyl alcohol full solubility occurs with a nitrate that has a nitrogen content as high as 12.3 per cent, whereas with the ethyl alcohol complete solubility occurs only in those cases where the nitrogen content is less than 11.2 per cent. More complete abstracts of each of the two articles by Kanamaru appear in the appendix.

Gibson and McCall (V-1) report on the viscosity of ether-alcohol solutions of nitrocellulose containing about 12.2 per cent nitrogen. Four per cent solutions were made at 20°C. The specific gravities of the ether and the alcohol were .72 and .817 respectively at 15°C. The following results were obtained:

% Ether by Volume	% Alcohol by Volume	Viscosity (Falling ball in seconds)
80	20	160.7
75	25	59.6
70	30	39.9
60	40	28.8
50	50	23.1
45	55	26.1
40	60	30.5
30	70	90.4

As the nitrogen content of the nitrocellulose increases, the percentage of ether in the mixture must be increased to obtain a minimum viscosity and this minimum viscosity also varies with the nitrogen content. The following table illustrates typical values:

% Nitrogen content	Minimum Viscosity (seconds)	Optimum ether:alcohol Ratio
11.8	31.8	50-50
12.2	23.1	53-47
12.55	7.6	70-30

Stettbacher (H-16) states that the most favorable mixture is one volume of ether of specific gravity .720 and one volume of alcohol when 99.5 per cent alcohol is used and that with a 95 per cent alcohol, maximum solubility occurs with the usual mixture of two volumes of ether and one volume of alcohol. There is no evidence in the reference that similar work was carried out with nitrates that contain as high as 13.4 per cent nitrogen. Stettbacher also states that the "high nitrated" cellulose can be gelatinized at low temperatures. No mention is made of the exact nitrogen content of the base material.

Medard (G-26) mentions a greatest gelatinizing effect with 65 parts of ether and 35 parts of alcohol but does not

state the water content of the alcohol.

In Alexander's Colloid Chemistry (Vol. IV. pp. 91) Storm reports that it has been found that when cellulose nitrate is immersed in dry alcohol or dry ether at temperatures ranging from $-80^{\circ}\text{C}.$ to $110^{\circ}\text{C}.$ very little swelling occurs. He cites an example where a nitrate film that was immersed in ether and also in absolute alcohol for several days increased its weight 28 per cent and 68 per cent respectively. When 5 per cent alcohol was added to the ether the weight increase was 75 per cent and more alcohol caused further increase. On the other hand, the addition of 2.5 per cent ether to the alcohol increased the swelling five-fold.

Masson (V-5) states that a fibrous cellulose nitrate absorbs both ether and alcohol vapors very readily. Absorption reached a maximum with equal molecular parts of alcohol and ether.

In some work done by Mardles (Q-1) he reports that he found that with solvent mixtures explored the rate of swelling is highest when the total swelling is greatest.

McBain (O-7) concluded from experimental data that with a given sample of nitrocellulose, solutions in various solvents show that the viscosity is inversely proportional to solvent power.

The heat of swelling has been taken as a criterion of solvent power. A. P. Okatow and S. I. Emmanuilowa (F-2) report a greatest heat of swelling of nitrocellulose found with a solvent containing equal parts of ether and alcohol and that the velocity of swelling and solution formation is

greatest at the boiling point of solid carbon dioxide. They also report that the swelling is favored by the application of pressure. They advise for best results a combination of low temperature, higher pressures and longer applications of pressure to obtain optimum swelling.

Fred Olsen (M-3) discusses the effect of the original fiber structure on the swelling of the nitrocellulose and points out certain differences in the behavior of cotton nitrate and wood cellulose nitrates.

Stettbacher claims that a given powder made from an acetone colloided nitrocellulose is denser and much less sensitive to moisture than one produced from an ether-alcohol colloid. He explains it by a better solvent action of the acetone on the high nitrated cotton, whereas ether-alcohol causes it to swell only. Again the exact nitrogen contents of the base product are not mentioned.

Stettbacher refers to Berl (Die Schiess und Sprengstoffw., 1933) who correlates the ease of nitrocellulose swelling with the degree of which the nitrocellulose has been depolymerized. He states that a low molecular weight nitrocellulose is much more susceptible to swelling than others of the same nitrogen content.

Medwedew (H-7) mentions work done to fractionate nitrocellulose into several portions by adding acetone water mixtures to ether-alcohol solutions of the nitrate. No reference is made to the solubility of the several portions so prepared.

Demougin (H-4) points out that nitrocellulose solubilities can be effected by a semi permeable membrane of the lesser

soluble nitrocellulose that remains on the outside of a fiber aggregate and that one can obtain higher solubilities by making the interior portions more readily available.

K. Atsuki and Ishiwara (H-14) examined nitrocellulose that had been gelled and cast into films. X-ray study was made. A 13 per cent nitrogen product admixed with nitroglycerine when converted into film by means of acetone solvent and by ether-alcohol solvent showed a more uniform structure with the acetone than with the ether-alcohol. The latter film appeared as a network structure with inner distorted and heterogeneous distribution of the molecular surface contact. They state that on drying an acetone solution of nitrocellulose, the solute may be kept in a state of dispersion until the amount of acetone becomes very little and this residue now adheres to the nitrocellulose as a molecular compound. In the ether-alcohol solution the ether evaporates first and the solute becomes insoluble, remaining in a swollen state during drying. It seems that the gel of the more depolymerized products are more regular in crystalline properties and that the crystal unit is smaller. He quotes Trillat that the cellulose nitrate of nitrogen per cent above 12.95 has a more marked crystalline character than a lower per cent nitrogen material.

Sacharov (F-4) discusses the application of ether-alcohol in the manufacture of smokeless powder and gives a complete example of the ether-alcohol balance. The original may contain some information more specific to the problem at hand.

Except in the case of mixed base explosives such as typified by cordite which contains nitroglycerine, acetone is not

ordinarily used to colloid nitrocellulose preparatory to its extrusion. It is stated in the literature that a single base colloid prepared with acetone as a swelling agent yields a smokeless powder that is brittle and hence dangerous. Experimental mention is made of a substitution of methyl alcohol for the ethyl alcohol in the ether-alcohol mixture but no evidence was found to show that the methyl alcohol has been used commercially. Except for a few cases cited above, no important attempt to change the ether-alcohol ratio appears either in the literature or in the discussion with the several technologists who were interviewed. The acceptance of the usual ratio of two volumes of ether to one volume of alcohol seems complete and there may be very good reason for it. It is conceivable, however, that this mixed solvent may be ideal for the well known cotton nitrates and not best suited for wood cellulose products or that the present day greater availability of anhydrous alcohol may change the situation. It is expected that any new program of work will include some study of other mixtures and of other solvents. Solvents that have come into general use in the past decade may offer a better means for colloidizing nitrocellulose. New combinations of old and new solvents may possess properties that can cause an improvement in colloid quality or they may permit a much more rapid production of material.

An early mention of a large number of esters, amines, ketones, and alcohols is made by Marquoyrol and Florentin (U-1). They mention a list of gelatinizer patents since 1900. T. Davis (T-1) reports on sixteen agents that were

studied in 1922. Zimmer (D-15) discusses more fully the solubilizing power of the lower alcohols. His base material was for the most part nitrocellulose of 13.5 per cent nitrogen content. His reagents included ether, benzene, acetone, ethyl acetate and their mixtures. He reports that in general the degree of swelling was greater the higher the molecular polarization of the liquid. The more the nitrocellulose swells in these organic liquids, the higher the charge on the nitrocellulose.

Some work has been done by the French to perfect a method for determining the plasticity of nitrate mixtures made during the manufacture of Poudre B. This composition contains two grades of nitrocellulose with 12.0 and 13.2 per cent nitrogen of which they consider the first soluble and the second insoluble in the mixture of ether and alcohol that is used. The test was developed to control uniformity of plasticity. In brief the procedure was as follows:

The mixture of nitrates and solvent was pressed into a block by means of a plunger in a metal cylinder. A metal rod of specified diameter and weighted was inserted through the top of the cylinder so as to rest on the colloid block. The penetration during a given time was taken as a measurement of plasticity. Abderhalden used this test with Poudre B and by his experiments found that the coefficient of plasticity reached a maximum when the proportion of "soluble" and "insoluble" nitrocellulose was 40 to 60. The plasticity increased as the amount of solvent was increased.

A. J. Phillips at Picatinny Arsenal contributed a full

chapter in Alexander's Colloid Chemistry, Vol. IV, on the structural variations in smokeless powders. The entire account deserves careful review in anticipation of a new experimental program. He points out that in a smokeless powder the nitrocellulose is incompletely gelatinized and that only part of that fraction that is gelatinized is dispersed. It is stated that nitrocelluloses vary greatly in their dispersability. Experiments are cited and photographs illustrate the vast difference in structure of films that were made from 8 per cent solutions of several commercial nitrates. The nitrates contain 12.6 per cent nitrogen and the solvent was the usual ether-alcohol mixture. Even in the presence of much larger percentages of solvent than are employed in smokeless powder manufacture, there is evidence of much undispersed material which stands out very clearly in the case of some of the products so examined.

Phillips emphasizes the importance of the dispersability of nitrocellulose and defines the term as the property which determines the ability to disperse under proper conditions. He also stresses the fact that in smokeless powder manufacture the restriction in time of contact and in amount of solvent applied makes it impossible to reach the maximum dispersion that could be attained under more favorable conditions. Pyrocotton contains soluble, partially soluble, and insoluble components; in other words, readily, slowly, and non-dispersable materials. Under usual conditions with a reduction in solvent percentage and time of contact the difficulties are exaggerated.

Phillips also shows photographs to illustrate the

chapter in Alexander's Colloid Chemistry, Vol. IV, on the structural variations in smokeless powders. The entire account deserves careful review in anticipation of a new experimental program. He points out that in a smokeless powder the nitrocellulose is incompletely gelatinized and that only part of that fraction that is gelatinized is dispersed. It is stated that nitrocelluloses vary greatly in their dispersability. Experiments are cited and photographs illustrate the vast difference in structure of films that were made from 8 per cent solutions of several commercial nitrates. The nitrates contain 12.6 per cent nitrogen and the solvent was the usual ether-alcohol mixture. Even in the presence of much larger percentages of solvent than are employed in smokeless powder manufacture, there is evidence of much undispersed material which stands out very clearly in the case of some of the products so examined.

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Phillips also shows photographs to illustrate the

heterogeneous structure of powder grains and explains the peculiar markings by more rapid shrinkage in the case of those portions which have present the more soluble constituents of the nitrocellulose. In many instances the uneven structure is probably responsible for changes in physical strength that occur on drying and on standing.

Note:

The questionnaire is submitted to indicate the type of questions that occur. Some entries may stimulate further thought.

QUESTIONNAIRE

1. It is common practice to use ether-alcohol (2 vol. plus 1 vol.) for the colloidizing agent both for the pyrocotton (12.6 per cent nitrogen) and for the mixture of nitrates (80 per cent of 13.4 per cent nitrogen plus 20 per cent of 12.6 per cent nitrogen). One investigator, Kanamaru, shows that less ether can be used satisfactorily with the high nitrogen products. If a reduction in ether content has some economic or processing advantage, then more work is necessary to determine the lower limit. Is there anything to be gained by substituting other solvents? What improvements might be attained? What is the criterion of an ideal solvent?
2. What is known about the use of anhydrous alcohol as one of the constituents of the solvent? Some early work in the references is sufficiently interesting to warrant further study particularly since anhydrous alcohol is now commercially available.
3. What is known about the use of methyl alcohol in the ether-alcohol mixture? Assuming that it functions satisfactorily, is there any economic or other reason why it should or should not be considered? Kanamaru's work suggests that the methyl alcohol may possess some advantage as a swelling agent.
4. Acetone colloids well but it is reported that, except with nitrocellulose-nitroglycerine powders, the powder is brittle. Is this brittleness the result of less residual solvent than

in the case of the ether-alcohol processed powder? If so, it appear that the alcohol is more firmly held by the nitrocellulose? If acetone has advantages in the processing (colloid-ing and extrusion), can we successfully use a three component solvent of ether-alcohol-acetone? What is the compatability?

5. The amount of alcohol that is left in the cake of nitrocellulose after dehydration limits the percentage of ether in the mixed solvent if one holds to a given percentage of mixed solvent based on nitrocellulose. What is the objection to a modification whereby more mixed solvent is used and a corresponding adjustment is made in the die size to allow for greater dilution of nitrocellulose? If solvent recovery is efficient, would more solvent than currently used (approximately 100 per cent based on nitrocellulose) be helpful in the production of a powder? Have such experiments been done? In such a case one could alter the composition of the solvent by adding alcohol to the ether.

6. Continuing the above speculation of the influence of change in solvent composition, what can be done to cause a higher concentration of nitrocellulose in the press cake from the dehydrating press? In such event more leeway is possible to enrich the mixed solvent in respect to ether or to use a higher percentage of ether in the solvent during the initial stages of mixing by holding out the remaining alcohol until some time after the mixing of nitrocellulose is put under way. Would benefits result?

7. In the present process can one expect that a more homogeneous colloid is possible if the mixing is done at two temperature levels? Both types of temperature curves should be considered. Specifically, what would occur if the mix were made initially at 5-10°C. after which the mass is brought to 20°C.? Or is it conceivable that the reverse sequence would prove best? Gelling rates, uniform penetration of solvent into the nitrocellulose, and the effect of an initial jacket of nitrocellulose that surrounds ungelled material may play important roles.

8. It is probable that more is known than has thus far come to the surface in regard to the relative solubilizing power of solvent on the two components (12.6 and 13.4 per cent nitrogen) in an FNH powder. Is it possible that better results may be realized if each of the nitrates were colloided separately and then mixed? It would seem that by so doing, a wider and better choice of colloiding conditions could be made for each of the nitrates. To illustrate, it may develop that the ether-alcohol would prove best for the low nitrogen component and an acetone containing solvent or one that contains ethyl acetate may be better for the 13.4 per cent nitrogen material.

9. Is it conceivable that the colloid mixing step would be more satisfactory if the blend were made not with a solvent but with a solution of nitrocellulose in the solvent? Would a properly prepared lacquer made up from some of the 12.6 per cent nitrogen nitrate distribute satisfactorily with the major

portion of the fibrous nitrate to serve as a bond? How about extrusion and physical properties of the finished grain?

10. It seems likely that in the production of FNH powder the 13.4 per cent nitrogen product colloids with greater difficulty than does the 12.6 per cent component. What might be gained by planning the production so that deliberate means are established to impart a low solution viscosity to the high nitrogen component? Two separate and distinct nitrations are now practiced. It would be no great trouble to plan the nitrating conditions so that the one product would have low viscosity. Another approach would comprise the adoption of two celluloses, one of normal high solution viscosity, the other with considerably lower viscosity. It is quite within the picture to consider the second and larger requirement to be a wood cellulose. Experiments to determine the improvement in solubilizing effect that can be obtained with the low viscosity nitrates would indicate whether this approach has practical possibilities.

11. Exposed surface of material to be colloided must play an important role in the rate and the uniformity with which the nitrate is swollen. Can one devise a practical means for further reducing the fibrous nitrocellulose after dehydration and before or during the mix with the solvent? The disintegration accompanied by maceration may conceivably be done in a ball mill, or by means of a sharp jordan. It may prove that the entire mixing and pulverization step could be practiced in a chrome steel ball mill or in a rod mill.

12. If mixing of nitrocellulose and solvent were done in a sealed container, higher initial temperatures could be prescribed to favor a vapor penetration before gelling takes place. This assumes that gellation occurs more rapidly at the lower temperatures.

13. Is it impractical to provide for an intermediate storage of nitrocellulose after it has been discharged from the mixer? A continued contact with the solvent at a proper temperature may cause better and more uniform gelling before the press blending steps are practiced.

14. Although it is not at hand, some of the explosives laboratories must have data on the water residues that are present in the cake from the dehydrating press. If this water which must be thoroughly adsorbed within the nitrocellulose were removed, would the ether-alcohol solvent prove more effective? Use of a substantially anhydrous alcohol near the end of the dehydration step may be the answer. A vapor sweeping of the disintegrated cake with anhydrous alcohol vapors may constitute another approach.

15. In the manufacture of an FNH powder does the presence of the dibutyl phthalate and the dinitro toluol interfere with the colloidizing properties of the ether-alcohol? Would a sequence of additions of solvent and plasticizer prove beneficial?

16. Does wood cellulose nitrate behave differently from the cotton nitrates when colloidized because of a different

assortment of nitrates within the composite? Fractional separation of the composite mass by use of solvents would give an opportunity to learn more of the swelling properties of the several components.

17. Application of solvent vapors to the disintegrated nitrocellulose press cake may prove an effective means for assuring good distribution and uniform penetration of the nitrocellulose. This step could be practiced in a closed container with provision for a removal of air before the ether vapors or their equivalent are applied. In this connection it might be well to review the present day methods by which soda cellulose crumbs are xanthated. In this process the loose crumbs are gently and slowly tumbled in an octagonal vessel mounted on a horizontal axis. The vessel is freed of air by evacuation and a calculated quantity of CS_2 is added at about 20°C . Progressive vaporization takes place as CS_2 reacts with the soda cellulose. A loose fibrous structure of mass is maintained by controlling the temperature and by operating to minimize a compacting of the loose mass. Good penetration of CS_2 vapors is realized and there is a uniformity of reaction that would not be possible if the reaction were carried out in a machine that subjects the mass to rubbing and partial densification. This tumbling step suitably adapted to optimum conditions of operation may offer a means for improved mixing and penetration of solvents into nitrocellulose preparatory to the blocking press operation. Recovery of solvent from the octagonal churn would be a simple matter. If it proved advantageous one could use an excess solvent for a short period

and recover the excess by a subsequent application of partial vacuum. It is conceivable that by a more effective swelling of the nitrocellulose the extrusion could be done with less solvent present in the green powder.

Standard laboratory tumbling churns are available for experimentation.

18. A more uniform colloid operation may result if provision is made for steps by which

(a) the nitrocellulose is first exposed to an excess of solvent under conditions to favor perfect distribution and penetration;

(b) a subsequent removal and recovery of some solvent from the vapor or liquid soaked fibrous mass before the preliminary blocking press or the macaroni press is used;

(c) steps as normally practiced.

19. Orientation of nitrocellulose in the extruded strand determines the ratio of shrinkage with the axis and across the diameter of the cut powder when solvent is removed. It is probable that major variations in "web" shrinkage can be brought about with a given colloid by changing the speed at which the extrusion is carried out. One would also expect that a variation in per cent solvent that is used or a difference in fluidity of the colloid by reason of nitrocellulose properties will influence orientation and hence the ratio of "web" shrinkage to shrinkage in length of powder grain. The magnitude of the changes so produced could be measured both by linear measurements of the grain shrinkage and by X-ray.

Is orientation an important factor quite aside from control of grain size? May it have a significant influence on ballistics? Is orientation more marked in the case of the high viscosity nitrates, or does the greater fluidity of the low viscosity nitrate colloid offset the effect of shorter chain length?

20. Does solvent leave the green powder mostly through the circular ends in much the same manner as happens when water is expelled from wood or does orientation of the nitrocellulose in the extruded strand have but little influence on the main direction of solvent travel as it escapes? If the solvent escape is largely directional as suggested, then it may prove of interest to consider experiments in which the ratio of length to diameter of grain is decreased to allow an easier removal of solvent. This may prove important not only during the solvent recovery step but also during the final drying.

21. When the "wet" drying process is used to remove last portions of solvent, is the shrinkage of powder grain less than when the removal of solvent is practiced with warm air?

22. Is it possible to remove solvent from a green powder by extraction with a low boiling point liquid that is miscible with ether-alcohol and which is not a solvent for nitrocellulose? Would such a procedure reduce the time required for solvent removal and may overall recovery of solvent be greater than now experienced? What about overall shrinkage? The presence of plasticizers might introduce complications.

23. No progressive shrinkage data were found. Changes that occur in length, diameter and in web of powder as successive portions of solvent are removed may help to explain the irregularities that are occasionally noted in the overall shrinkage figures. For example, does the variation in final dimensions of the powder grains relate to differences in behavior that are found during the early stages of solvent removal or is it explained by differences that occur in the drying house near the last stages of solvent removal? In such a study the different rate of dimensional changes across the grain and in the length of the cylindrical units may prove significant.

24. Some technologists have expressed an opinion that the rate at which solvent is removed from green powder can influence the ultimate dimensions of the grain. This should be checked. If it is confirmed by fact, then it would appear that the solvent recovery schedules demand further standardization.

25. Nothing was found regarding the variations in density of the finished powder. If incomplete colloidizing of some of the nitrocellulose results in a less composite volumetric shrinkage of the powder grain, the density figure may be of help in the interpretation of what takes place under different conditions. Density of powder may become an important control test.

26. A great deal of work has been done in the field of suitable

plasticizers for the nitrocellulose. Plasticizers are not used in the pyrocotton powders that are made at Indianhead for Navy use. Can plasticizers be applied advantageously to such powders, and if so, will it be necessary to resort to a higher than 12.6 per cent nitrogen base?

27. Do the common plasticizers that are now used in the FNH powders function as swelling agents for nitrocellulose? Or do they serve as water repellent diluents only? This can probably be answered by those who have been close to the development of that type of powder.

28. It has been reported that it is sometimes noted that a green powder increases its diameter over a period of hours after it has passed through the die. Is this the result of improper mixing and blending of solvent and nitrocellulose prior to the extrusion of the colloided mass? Do some types of nitrocellulose require longer periods of time than others to swell fully with a given addition of solvent even though mixing is thoroughly accomplished? Is the post swelling across the diameter accompanied by an increase in total volume of grain or is there a corresponding shrinkage in length? In any event does post swelling cease to be a problem if sufficient time is allowed for full swelling to occur before extrusion is practiced?

29. Is the brittleness of a finished powder related to the amount of solvent that is allowed to remain? If reports are properly understood, it appears that the plasticizers (dibutyl

phthalate and dinitro toluol) do not automatically assure non brittleness. Some of the powder that was made from a wood cellulose base fractured on crushing more readily than the corresponding powder that was made from a cotton base even when the powders were of the FNH type. It would be worth while to establish a relationship of compressibility values and residual solvent in a range from 10 to 2 per cent. A very small added percentage of solvent may have a major effect on toughness.

30. There is a general belief that a low compressibility and a brittleness in powder that is made from wood cellulose base is related to a low solution viscosity of the nitrocellulose. It is conceivable that nitrated pentosans and hemicellulose may be equally or more responsible. A series of powders that are prepared from nitrates of wood celluloses that are typically rich and lean in alpha cellulose, and in pentosans, would enable the operator to extend his present knowledge. Likewise wood pulps of high and low viscosity and substantially alike otherwise would allow the opportunity to check up on the matter of effect of viscosity on brittleness of powder.

31. It has been stated that in some instances anhydrous acetone is not a satisfactory solvent for nitrocellulose and that some water is needed to favor swelling and ultimate solution. Very probably the need for some polar solvent is more pronounced in the case of the lower nitrogen products. There is a likelihood that when acetone is employed in a mixed

solvent that is intended for use with the high nitrogen products, the presence of an optimum percentage of water is of great importance. This deserves further attention.

32. Is the solvent power of a mixture indicated by the viscosity of the lacquer that is made up under standard conditions? Is there value in an experimental program in which a regular blend of 13.4 and 12.6 per cent nitrogen products is dissolved in a number of solvent mixtures with an object of establishing minimum viscosities in those cases where solution is substantially complete. Such an investigation may reveal not only the behavior of the several possible solvent mixtures but also the effect of addition of the several components of the mixtures in different sequence. Additional work may show advantages of using some other combination of nitrate blend to produce a desired average nitrogen level.

ABSTRACTS

A-3. T.Petitpas. J.Chim.Phys. 37,6-18 (1940)

Gelatinization of Nitrocellulose

Studies on the gelatinization of di- and trinitrocelluloses were made using both acetone vapor and liquid acetone diluted with an inert solvent. Regardless of extent of nitration, one molecule of gelatinizing agent for each C₆ group in the cellulose was a very important relation. Breaks in the vapor pressure curve, the appearance of the cellulose, and the X-ray diagrams agree. Beyond this value of one molecule gelatinizer to one C₆ group, the fibers begin to swell and visible changes occur until for 13.8 per cent nitrogen at about 3 molecules gelatinizer to one C₆ gelatinization is complete and dispersion occurs. The lower per cent nitrogen (11.85 per cent) behaves similarly. A small amount of nitrocellulose passes into solution at the point of gelling forming a coazervate. This gelling occurs when the NO₂ groups have been saturated with acetone.

A-4. O.Kratky. Angew.Chem. 53,153-62 (1940)

The Micellar Structure of Cellulose and of its Derivatives

A comprehensive modern review with 75 references and numerous diagrams of the micellar structure of cellulose derivatives including a discussion of swelling, solution and reprecipitation.

B-2. E.Berl and W.Koerber. J.Am.Chem.Soc. 61,154-7(1939)

Cellulose Compounds

The following table together with a number of photomicrographs (see original article) gives the results of swelling of nitrocellulose in various solvents at various temperatures:

Definition of symbols used:

- Fiber insoluble and unchanged.
- + Fibers lose original structure and form solid translucent lumps of the same refractive index as the solvent.

++ Fibers form a gel at low temperatures which consists of small soft translucent lumps. The gel does not change its consistency when warmed to room temperature. It is highly swollen and has a limited solubility in the solvent. After standing at room temperature 2 phases result: viscous gel covered by non viscous solvent.

+++ Completely dissolved, viscosity of solvent increases.

(+) Width of fibers enlarged by swelling.

Table I

Solvents	°C.	12.02% N	12.6% N	13.4% N	13.9% N
Ether	+20	-	-	-	-
	-50	-	-	-	-
Ethanol	+20	-	-	-	-
	-50	++	-	-	-
Ether-Ethanol 60:40	+20	+++	+++	-	-
	-50	+++	+++	++	+
Methanol	+20	+++	+++	-	-
	-50	+++	+++	++	++
Glacial Acetic Acid	+20	+++	+++	-	-
Ethylene Glycol	+20	-	-	-	-
Acetic Anhydride	+20	+++	++	++	++
Formic Acid	+20	-	-	-	-
Ethyl Acetate	+20	+++	+++	+++	+++
Methyl Acetate	+20	+++	+++	(+)	(+)
	-50	+++	+++	+++	+++

The ratio of ether to ethanol was varied considerably (2:1, 4:1, 2:3, 1:4). Two highly nitrated esters with 13.4 and 13.9 per cent nitrogen were practically insoluble in the different mixtures of ether alcohol at room temperature, only a slight swelling effect being observed. At -50°C. all the fibers disintegrated in these ether ethanol mixtures independent of the per cent nitrogen. It is concluded from these and other data that ethyl ether and ethyl alcohol do not form molecular compounds. A theory of the action of mixed solvents is briefly discussed which does not substantiate the theory of an oxonium compound formation.

B-8. L.Solier. Mem.Poudres 29, 49-68 (1939)

Notes on the Elimination of Solvent
from Powder B

Experiments are described dealing with the soaking of powders in saturated salt solutions and other materials. It is found that the loss in weight in drying is due chiefly to ethyl alcohol. The percentage of residual solvent increases with decrease in the strength of alcohol while the stronger the alcohol the greater the opacity and the lower the stability. Steeping in water without previous ethyl alcohol treatment showed poor elimination of ethyl ether. Much better results with respect to coefficient of emission and stability were secured on highly volatile powders when 1 to 10 per cent ether was added to the alcohol followed by steeping in pure water. Steeping in ethyl alcohol at 60°C. produced as rapid results as methyl alcohol at 30°C.

B-9. K.Kanamaru. Koll.Z. 87,191 (1939)

Aging Process of Nitrocellulose
in Various Media

Samples of 13.1, 12.82, and 12.61 per cent nitrogen were studied by X-rays and viscometric determinations during periods extending up to 459 days. Ethyl alcohol, carbon tetrachloride, benzol, and petroleum ether were used. The viscosities in alcohol and water for 13.1 per cent nitrogen go through a maximum after a certain time but in benzol and carbon tetrachloride very little change takes place, this being due to the non-polar character of the substances. The denser the gel structure, the more difficult the swelling or solution process and the stronger the increase in the viscosity of the sol obtained.

C-5. A.K.Doolittle. Ind.Eng.Chem. 30,189-203(1938)

Solubility Power of Nitrocellulose Solvents

This paper deals with a compound of 12.08 per cent nitrogen for lacquers but the wide range of solvent mixtures studied and the methods used (toluene dilution ratios, viscosities of solutions of nitrocellulose in the solvents and mixtures, and phase diagrams which provide a complete evaluation of solvent strength by combining both dilution ratio and viscosity data) are of general interest and may well have application to the higher nitrated products.

C-6. K.Kanamaru and J.Chao. Kolloid Z. 84,85-99(1938)

The Sorption of Vapors of Various Fluids
by Cellulose and its Derivatives

Nitrocellulose of 13.53 per cent nitrogen in the form of fibers and film was exposed to vapors of methyl, ethyl, n-propyl, n-butyl alcohols, ethyl ether, acetone, benzene, acetic acid, and chloroform. It is found that the amount of vapor adsorbed is not always in relation to the solubility in the liquid probably due to the secondary factors involved (diffusion of liquid into the gel structure, breaking up of the gel structure, Brownian motion, etc. while dissolving). On the other hand, a film of gel forms on the outside of the nitrocellulose when exposed to the vapor, also introducing a secondary factor whose effect apparently need not be the same as that of the liquid. The amount of vapor adsorbed decreased in the following order: (1) acetone, (2) water, (3) methyl alcohol, (4) acetic acid, (5) butyl alcohol, (6) ethyl ether. Ethyl alcohol was not studied. The data agree with the zeta potential determinations of the effects of the pure solvents on nitrocellulose.

C-7. H.M.Spurlin. Ind.Eng.Chem. 30,538-42 (1938)

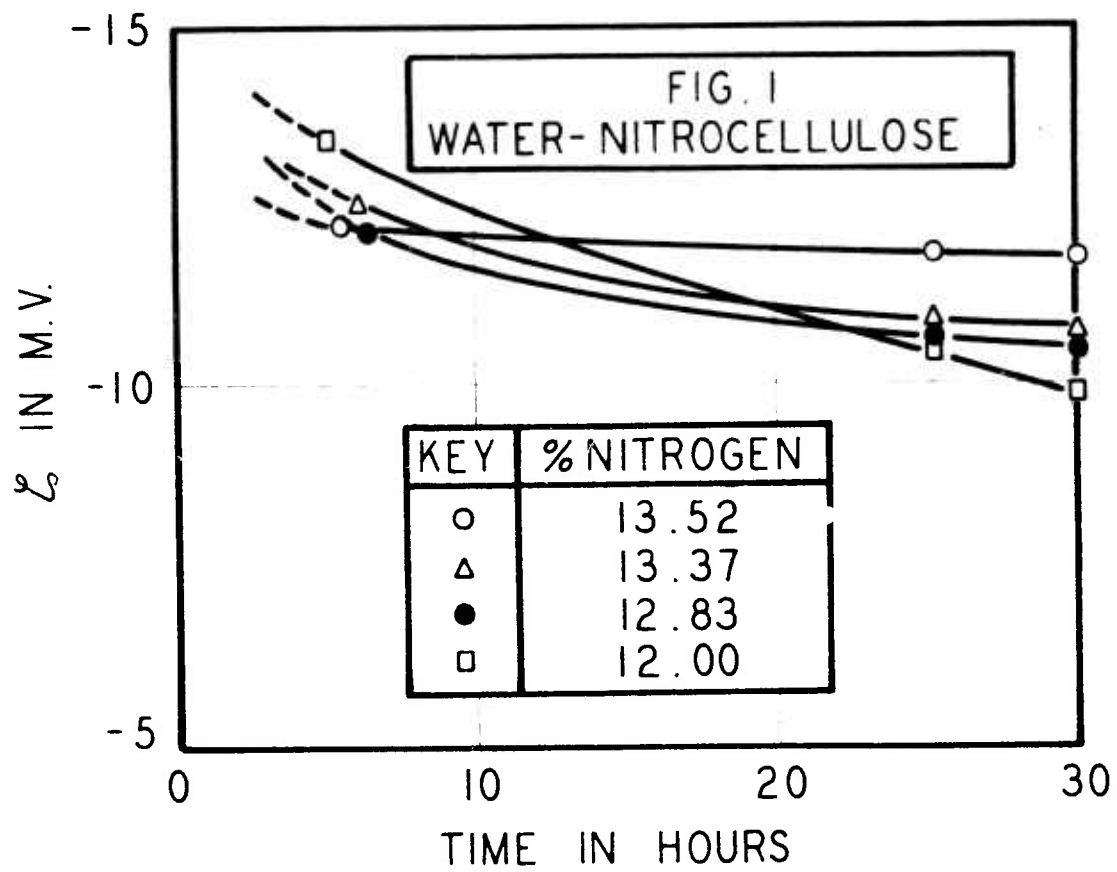
Influence of Homogeneity on the
Properties of Nitrocellulose

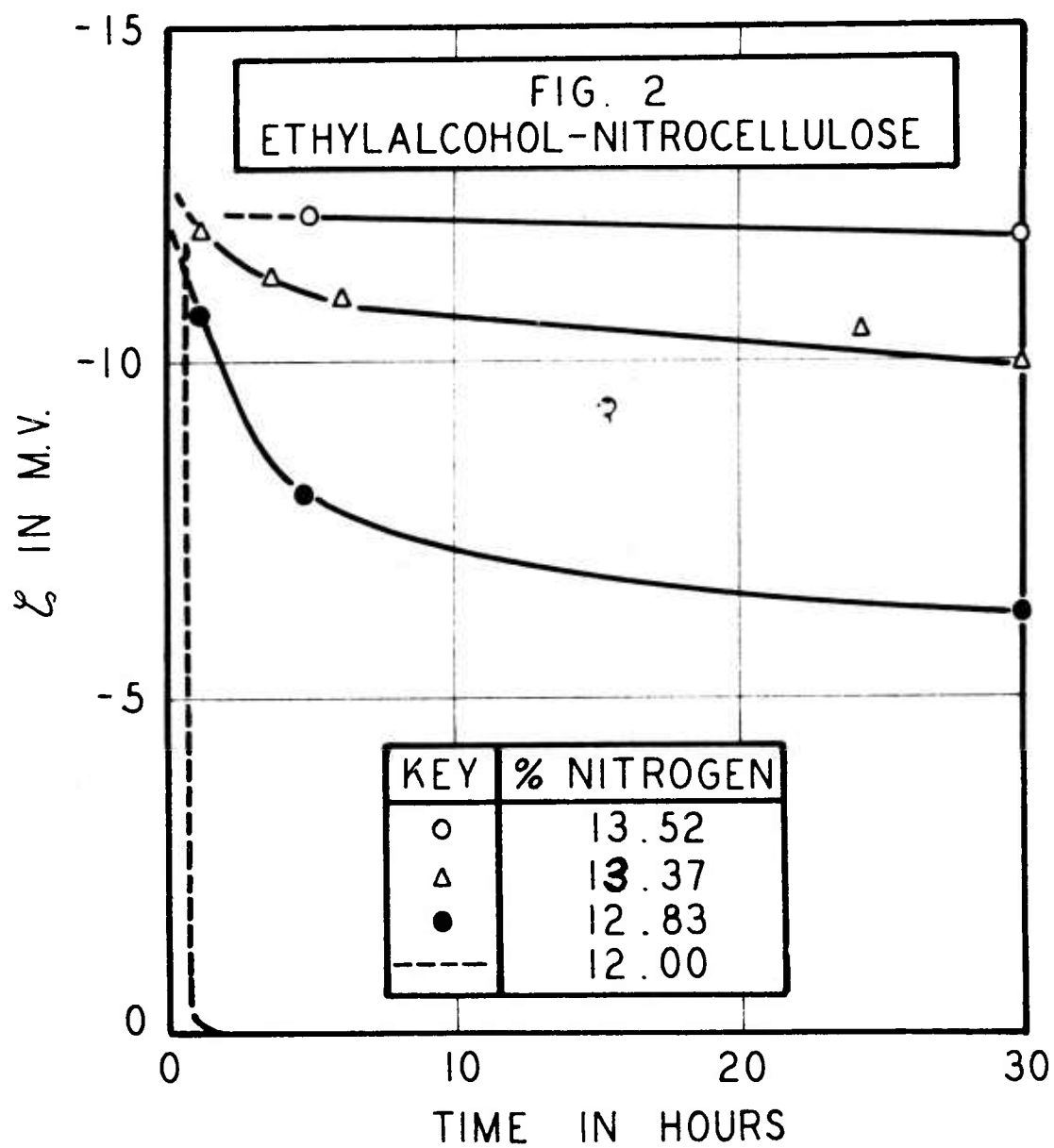
This paper deals with the careful fractionation of a 12.05 per cent nitrogen nitrocellulose. It is shown how the viscosity is a function of the particle size distribution; the pure fractions are better than ordinary cellulose derivatives and blends.

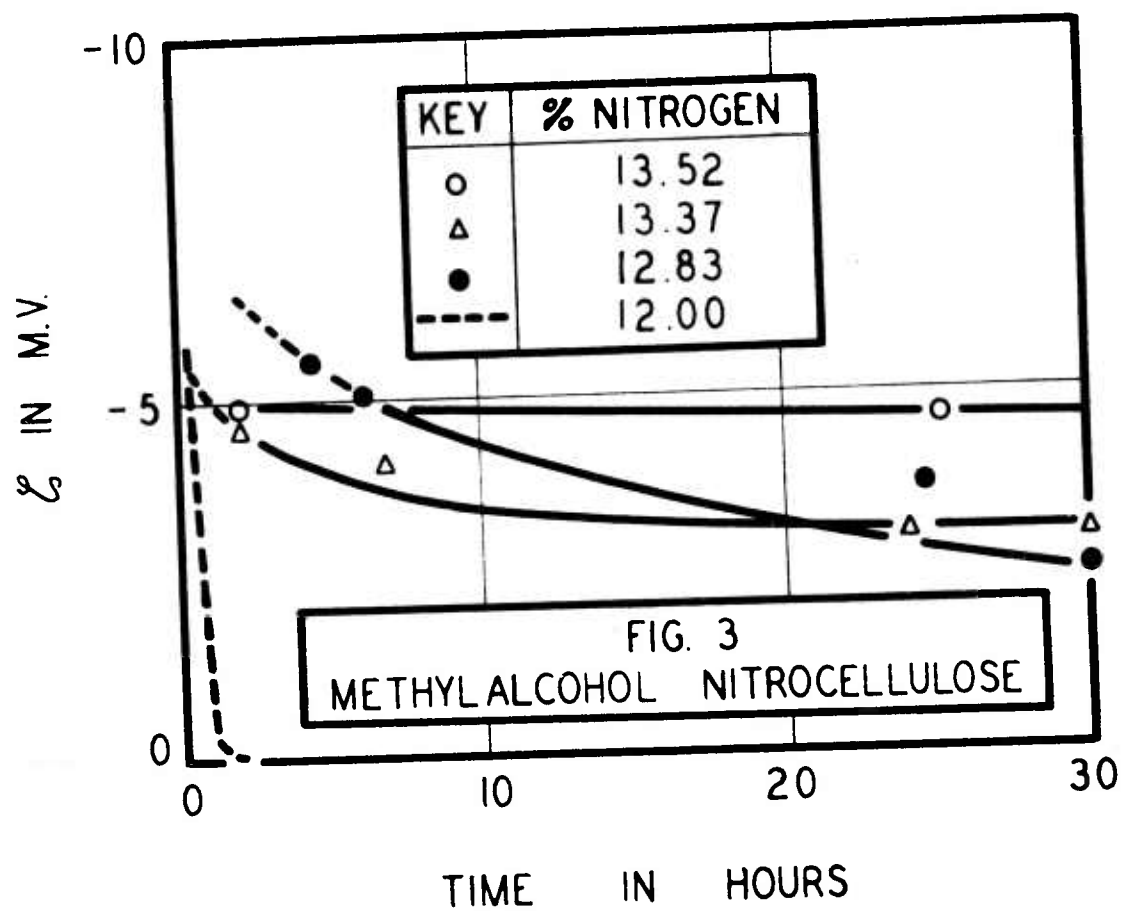
C-11. K.Kanamaru, T.Takada and K.Maeda. J.Soc.Chem.Ind., Japan
(Suppl.) 40,153-9(1938)

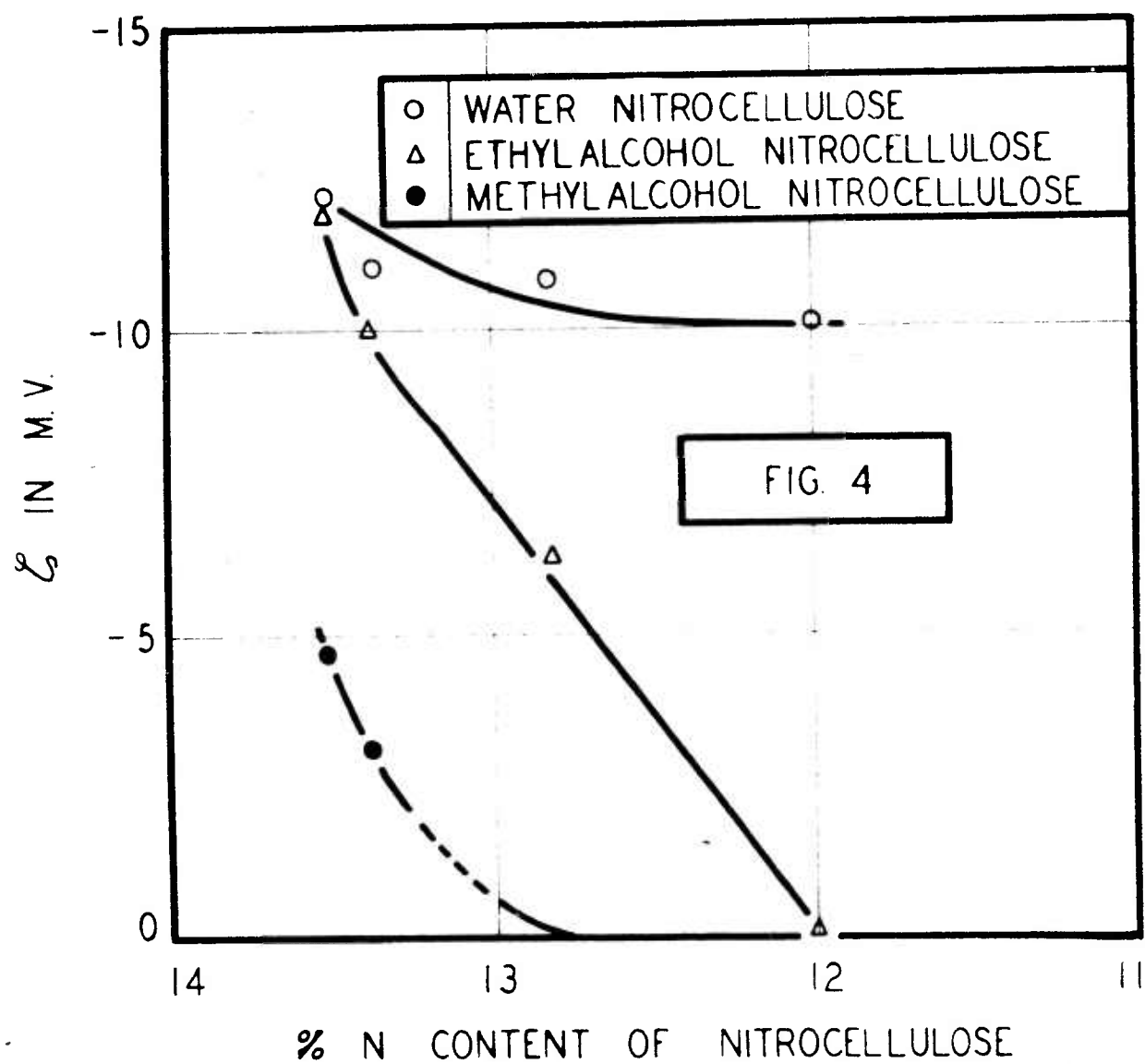
The Zeta Potential of Nitrocellulose

Nitrocelluloses of 13.52, 13.37, 12.83 and 12.00 per cent nitrogen were prepared from ramie and carefully purified. The authors point out that previous attempts to correlate properties of the fluid (e.g. dielectric constant, dipole moment, etc.) with swelling behavior on organic lyophilic materials have been made but all have been severely limited. The Zeta potential correlation presented here, because it includes the properties of both dispersoid and dispersion medium, is more satisfactory. It is found that Z_0 (the Zeta potential immediately after immersion) is higher the stronger the swelling capacity of the liquid for the nitrocellulose; Z_{∞} , the limit of the Zeta potential, is lower the higher the degree of swelling of the nitrocellulose. The nitrocellulose has a zero potential in that state in which the nitrocellulose is









so strongly solvated that the degree of swelling approaches solution.

The solubility of nitrocellulose in the liquids studied decreases in the order: methyl alcohol, ethyl alcohol, water. Methyl alcohol dissolves completely nitrocellulose of less than 12.3 per cent while ethyl alcohol dissolves nitrocellulose of less than 11.2 per cent nitrogen. The figures 1 to 4 show how the curves of Zeta versus time confirm the above generalizations. The following table gives a summary of the correlation of relative change in the Zeta potential with swelling action:

Swelling agent	% N	$\frac{Z_0 - Z_\infty}{Z_0} \times 100$	Swelling of the Nitrocellulose
H ₂ O	13.52	1.3	Doesn't swell
	13.37	11.9	Doesn't swell
	12.83	11.0	Doesn't swell
	12.00	24.9	Weak swelling
Ethyl Alcohol	13.52	1.2	Doesn't swell
	13.37	16.1	Weak swelling
	12.83	40.6	Swelling
	12.00	Very large	Strong swelling
Methyl Alcohol	13.52	5.8	Weak swelling
	13.37	33.2	Swelling
	12.83	50.2	Strong swelling
	12.00	Very large	Soluble

Curve 4 shows values of Z_{00} versus per cent nitrogen.

D-1. A.Douillet and Ficherouille. Mem.Poudres 27,115(1937)

Gelatinizers for Guncotton

Douillet et al state that methyl, ethyl, propyl, butyl and amyl oxalates are excellent gelatinizers for nitrocellulose. It appears that they gelatinize guncotton at ordinary temperatures. This is contrary to the usual assumption that the esters of the dibasic acids are good gelatinizers for nitrocellulose only if the two carboxyl groups are not close to one another in the molecule.

D-2. K.Kanamaru and S.Ueno. Kolloid Z. 79,77-91(1937)

Electrokinetic Examination of the Lyophilic Properties of Cellulose Derivatives

13.5 per cent nitrogen was studied in alcohol, ether, benzene, acetone, ethyl acetate, as well as mixtures of these fluids, by the method of the Zeta potential determination (streaming potential). The degree of swelling decreases in the order: alcohol, ether, benzene. The Zeta potential measurements were compared with direct measurements on the degree of swelling Q, expressed as grams solvent taken up by 100 grams dry nitrocellulose film. Curves were drawn of both Q and Z as a function of time and of composition for mixtures of ether-alcohol (0 to 100 per cent), ether-benzene (0 to 100 per cent), ethyl alcohol-benzene (0 to 100 per cent), acetone-benzene (85 to 100 per cent benzene), ethyl acetate-benzene (65 to 100 per cent benzene). The following table shows values of Q obtained:

Ethyl Alcohol-Ether

Time After Dipping Hrs.	2.0	10.0	14.	20	34	74	124	179	268	420
Vol. % Ether										
0	1.1			6.7	8.0	8.5	8.7	9.0		9.2
20	1.6			13.4	19.5	32.0	34.2	26.1		36.3
40	19.8			47.7	50.8	53.6	61.8	66.0		73.1
60	7.2			40.0	45.1	46.3	48.9	50.1		57.5
80	1.7			15.2	21.5	26.4	26.5	26.5		26.5
1000	0.3			1.6	2.1	2.1	2.3	2.8		2.8

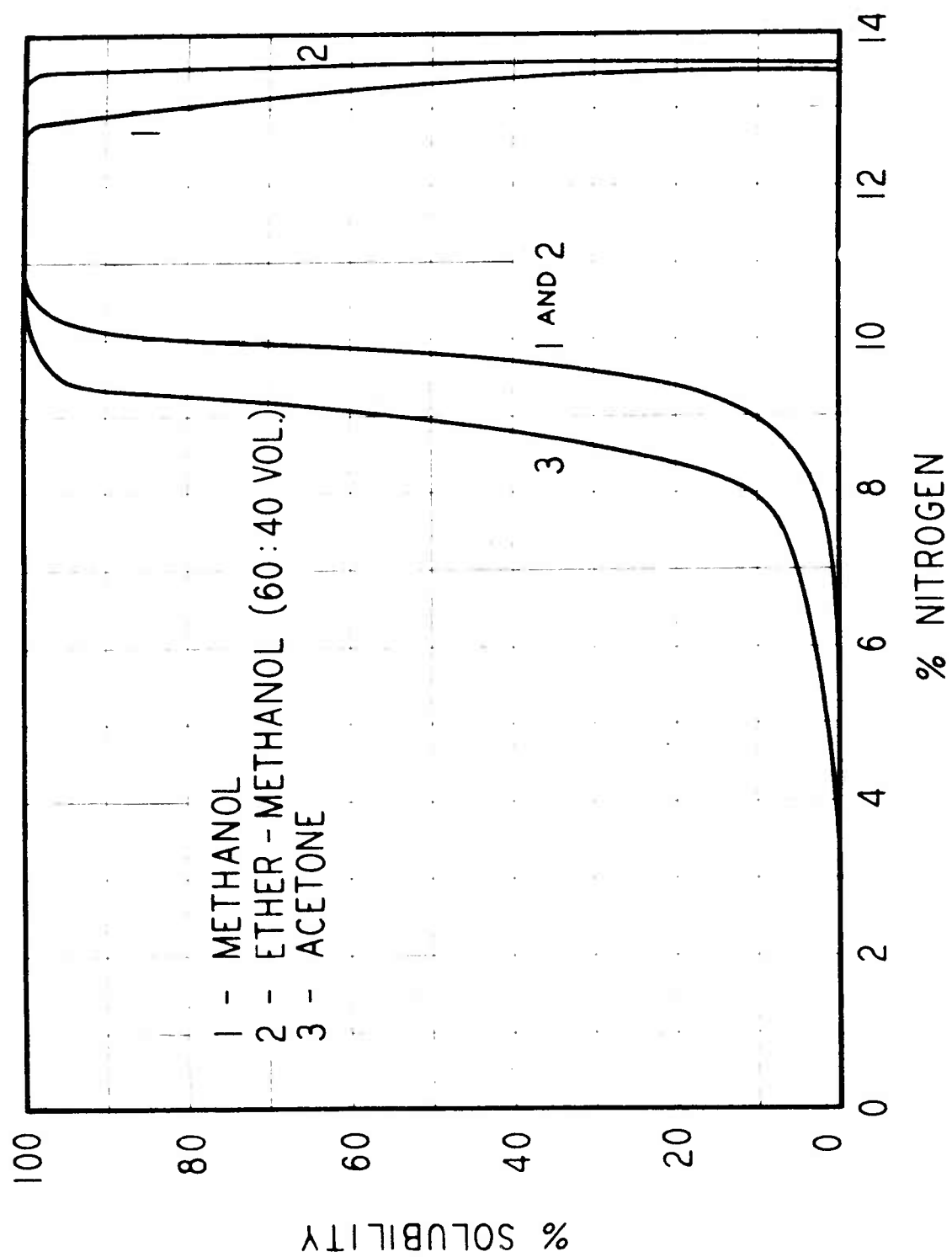
Acetone-C₆H₆

Vol. % C ₆ H ₆										
85	25.1	91.0	96.7		99.1	100.0	101.5	101.6	105.2	108.2
88	11.20	22.50	24.31		25.41	28.48	29.72	31.50	32.50	32.5
92	0.98	3.95	5.00		8.28	9.73	10.02	11.10	11.87	11.91
96	--	--	1.56		2.70	2.80	2.90	2.92	3.10	3.19

Ethyl Acetate-C₆H₆

Vol. % C ₆ H ₆										
65	78.0	145.50	153.52		162.67	165.0	167.89	170.18	178.64	181.20
73	27.23	49.98	54.24		56.10	63.76	69.00	73.49	75.50	76.00
82	0.18	1.17	1.51		12.27	14.00	14.24	16.20	16.79	16.92
91	0.13	1.00	1.32		1.54	2.59	3.70	4.80	5.45	5.31
1000	--	--	--	0.10	0.12	0.13	0.13	0.14	--	0.15

Due to the difficulty of measuring the initial values of the Zeta potential in very strong solvents, the flatness of the curve for ether-alcohol mixtures, for example, as compared



with the curve for Q , may be explained. However, there is a good correlation between the ration $\Delta Z/Z$ and Q .

Ether-Alcohol	$-\Delta Z$	$-\frac{\Delta Z}{Z}$	Q
Vol % Ether			
0	2.37	6.63	9.2
20	35.45	79.43	36.5
40	40.67	87.46	73.1
60	31.80	84.42	57.5
80	4.45	45.17	26.0
1000	0.00054	4.00	2.8
Acetone-C ₆ H ₆			
Vol % C ₆ H ₆			
85	0.2488	29.90	100.50
88	0.0508	15.39	29.72
92	0.000092	12.11	10.02
96	0.000072	2.89	2.90
1000	0.000000	0.	0.15
Ethyl-acetate-C ₆ H ₆			
Vol % C ₆ H ₆			
65	0.5037	52.87	167.89
73	0.1053	32.27	69.00

It is concluded that at least qualitatively this value of $\frac{Z_0 - Z_\infty}{Z_0}$ is a measure of the solvation capacity. It is

further stated that when nitrocellulose is immersed in a mixture, the two components diffuse into the micellar structure at different rates and hence the layer of liquid at the interface is different from that of the main body. With time equilibrium sets in. The quicker the swelling, the quicker the micelle is broken down and therefore the quicker the equilibrium is reached. This might indicate that treatment with the less active component, e.g. ether before alcohol, might result in quicker swelling.

D-4. K.Hess and W.Philippoff. Ber. 70,639-55 (1937)

The Viscosity of Organic High Polymers as Related to Concentration

This paper is a long critical survey of the correlations

of viscosity with concentration, type of polymer, etc. Measurements are cited for trinitrocellulose, collodion, etc. and an equation correlating the data is presented.

D-5. S.Rogowin and W.Iwanowa. Colloid J.(USSR)3,309-19(1937)

Study of the Solution Process of
Cellulose Derivatives - III

S.Rogowin et al go into the theory of mixtures of solvents with non-solvents, particularly in respect to their action on the lower nitrogen containing products. This paper has in mind mostly the lacquer industry but the findings may justify further study to see whether the data can be partly extrapolated in the high nitrogen field.

D-6. I.O.Goldman. Kinofotokhim.Prom. 35-43 (1937)

Properties of Acetone-Alcohol Cellulose
Nitrate Solutions

Goldman discusses the use of acetone-alcohol mixtures to replace the usual ether-alcohol mixture. He indicates less loss of solvent in storage and emphasizes a lower fire hazard. The work was done primarily in the film field. Whether the low nitrogen product results can be translated to the higher nitrogen fields is not clear.

D-7. A.A.Morozov and A.V.Pamfilov. J.Gen.Chem.(USSR)7,2154-66 (1937)

The Theory of Change of Viscosity of
Nitrocellulose Solutions

Morozov et al study the theory of viscosity change of nitrocellulose solutions. The study includes work with 13.2 per cent, 12.1 per cent, and 10.4 per cent nitrogen. The author apparently discounts the theory of viscosity reduction by depolymerization and discusses the breaking down of the internal structure of the solution, that is, the lowering of its elastic properties.

D-8. W.Coltor. J.Soc.Chem.Ind. 56,363-75 T (1937)

Solubility Properties of Certain
High Polymeric Substances

An extensive theoretical discussion of swelling and

dispersion is presented with an explanation of why certain mixtures of solvents have a very beneficial effect as compared to the pure solvents. Experimental data on cellulose acetate, ethyl alcohol, etc. are given. The article deserves further study.

D-9. H. Staudinger and M. Sorkin. Ber. 70B, 1993-2017 (1937)

Highly Polymeric Compounds
Viscosity Investigation of Cellulose Nitrate

Staudinger et al studied the viscosity of sols, gels, and concentrated solutions of nitrocellulose containing 12.7 to 13 per cent nitrogen in acetone and butyl acetate.

D-11. S. Papkow, S. Rogowin, and W. Kargin. J. Phys. Chem. (USSR)
10, 156-7 (1937)

Solubility of Cellulose and its Esters

S. Papkow et al go into the solubility of cellulose and its esters in organic liquids. From their data it seems that the systems in question follow the laws of binary liquid systems. It is not evident without further search through the original article whether this work deals primarily with the low nitrogen products.

D-12. I. Sakurada and N. Saito. Kolloid Z. 81, 208-12 (1937)

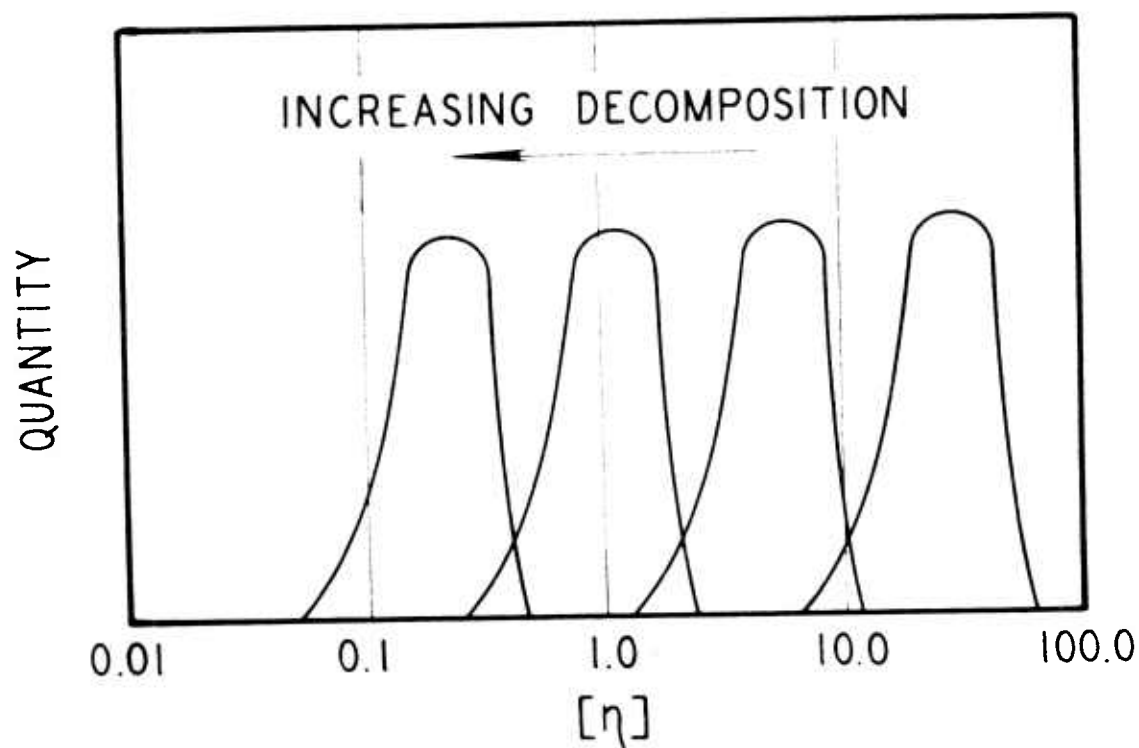
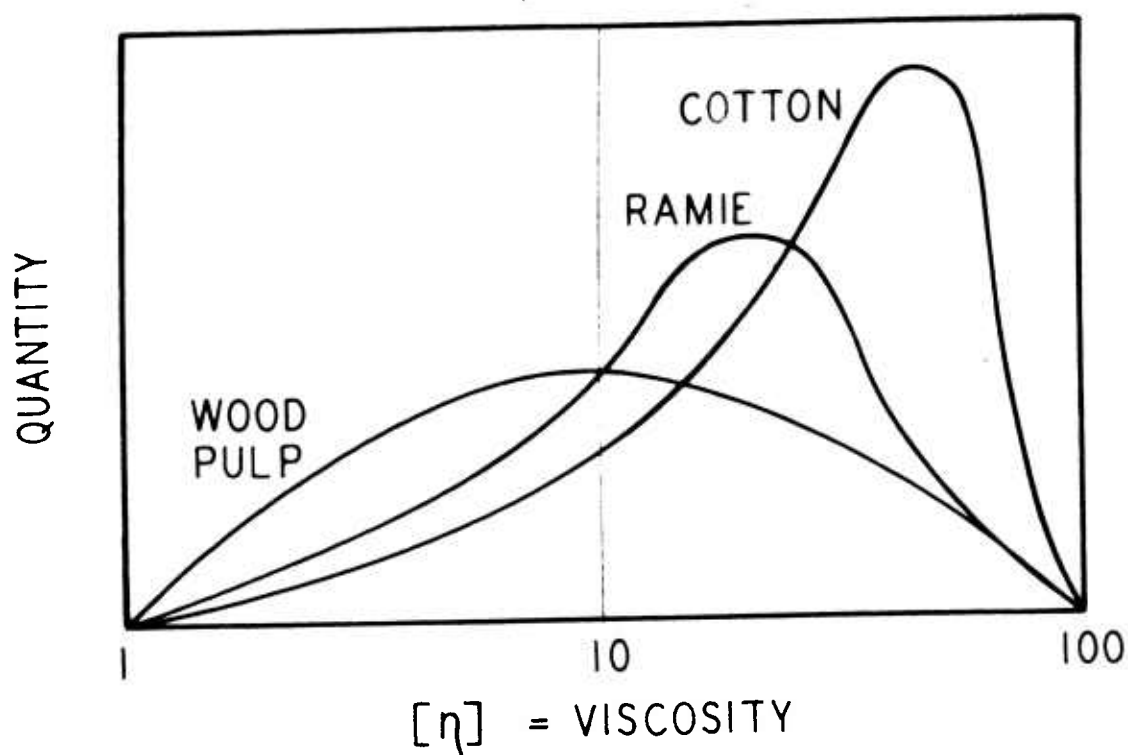
A Simple Overflow Viscosimeter and its Use in
Determination of Solubilizing Power of
Organic Liquids for Cellulose Esters

The instrument is used to show relative viscosities of a solution containing a cellulose derivative on addition of a solvent, a diluent, or a precipitation agent. Examples with nitrocellulose are given.

D-13. W. Philippoff. Ber. 70, 827-38 (1937)

Mixing Experiments and the Influence of
Hetero-Dispersion on the Flow Curve
of Organic High Polymers

Experiments with trinitrocelluloses of 13.90 and 13.74 per cent nitrogen are given involving viscosity and fluidity curve measurements in butyl acetate and dioxan. The curves of mixtures of high viscosity and very low viscous



SCHEMATIC REPRESENTATION OF
ACTION OF BLEACHING ON DISTRIBUTION
CURVE OF COTTON

trinitrocellulose and those of trinitrocellulose which is obtained by chemical treatment, i.e., decomposed by bleaching and shows the same viscosity as the mixture, are different. The effect of the initial bleach is traced on the viscosity curves. The chemical decomposition can therefore not consist in the conversion of a very high viscous material into a low viscous material since mixtures of 2 preparations of varying viscosity give flow curves which are different from the intermediate preparation of the same viscosity. The polydisperseness of high molecules is given by distribution curves. The influence of the origin of the cellulose on the viscosity properties depends on a different distribution curve. The mixing law can be given in the form $[\eta]_m \cdot C_m = \sum [\eta]_i \cdot C_i$, where $[\eta]_m$ is the relative viscosity of the solution of concentration C_m and $[\eta]_i$ and C_i are the viscosities and concentrations of the individual components making up the solution. Thus it is seen that an interaction of the components never results in a lowering of viscosity -- the viscosity of the mixture is always higher than the highest viscous compound used. The decomposition or bleaching process, therefore, does not change the shape of the distribution curve but moves it to lower average viscosity.

D-14. G.V.Schulz. Naturwiss 25,346-47 (1937)

Swelling Measurements on Polymer-Homologous Nitrocelluloses

Theoretical studies involving measurement of the vapor pressure lowering in gels of nitrocellulose in acetone are presented.

D-15. F.Zimmer. Farben Ztg. 42,438 (1937)

Influence of Solvent and Non-Solvent on Nitrocellulose Molecule

Zimmer discusses the solubilizing power of methyl alcohol and ethyl alcohol on nitrocellulose. The discussion relates largely to the mechanism whereby solvents act upon nitrocellulose. Comparison is made with some of the higher alcohols.

D-17. Lacape and Jourdin. Mem.Poudres 27,162-78 (1937)

Examination of Solvent Residues in Powder B

Lacape et al go into the progressive elimination of residual solvent from the powder grain. It is pointed out that ether is eliminated rapidly at first and then very slowly while alcohol is eliminated at a regular rate. Steeping in water rapidly reduces the content of alcohol and ether but at parallel rates.

E-1. J.Scheiber and O.Baier. Kolloid Beihefte 43,363-416(1936)

The Solution State of Film-Forming Materials

Scheiber states that butyl acetate is a better solvent for nitrocellulose than either acetone or ethyl acetate even though the absolute viscosity of its solution may be higher.

E-3. M.Ishihara. J.Soc.Chem.Ind., Japan 39, Suppl. 62-5, 65-8, 68-70
70-74(1936)

The Structure of Cellulose Nitrates

Ishihara reports on x-ray work done with nitrates containing in the main high percentages of nitrogen. Some of this work was done with nitrates produced from unusual materials such as hemp. Some work is directed toward the gelatinized nitrocellulose.

E-4. I.Sakurada and A.Kotera. Cellulosechemie 17,130(1936)

Changes in Viscosity Properties of Nitrocelluloses

Sakurada et al study changes in viscosity of nitrocellulose solutions with concentration. Some discussion is directed to a speculation on the shape of the dispersed nitrocellulose particles in the solution. Sketches are included.

F-2. A.P.Okatow and S.I.Emmanullowa. J.Appl.Chem.(USSR) 8,
1248-64 (1935)

Study of the Interaction of Cellulose Esters and their Solvents

Nitrocellulose of 12.38 and 13.3 per cent nitrogen was studied. The interaction of cellulose nitrates with various solvents proceeds in three steps: wetting, swelling, and sol formation. The wettability depends on the chemical and physical properties of a nitrocellulose and a solvent. A solvent penetrates the capillary orifices and intermicellar cavities formed in wetting and forms solvate films in and about the micelles causing their distention. The formation of thin solvate films results in a limited gel swelling. If, however, the solvation proceeds energetically forming films of such dimensions that the intermicellar forces of attraction become insignificant, then the micelles are uniformly distributed by diffusion in the liquid, forming a sol. The osmotic pressure within the gel, caused by the solution of a certain part of the gel in the capillaries and intermicellar cavities, is also probably an important factor. The heat of wetting of cellulose nitrate showed that the greatest thermal

effect results with a mixture of ethyl alcohol and ether in equal proportions and the thermal effect decreases with increasing ratio of ether in the mixture. The minimum thermal effect is obtained with ether alone which for highly nitrated nitrocellulose is negative. These results indicate the chemical nature of the interaction of nitrocellulose with a solvent. From thermodynamics swelling should be more energetic at low temperatures and high pressures. This was found to be the case. The greatest rate, at the boiling point of solid carbon dioxide, was with equal mixtures of ethyl alcohol and ether, which decreases gradually with increasing ether. It follows that by interaction with solvents, there is a limited swelling of one part of the cellulose nitrates and sol formation of another. In pressing, a further swelling of the insufficiently swollen gel at the expense of the solvent content in the highly solvated micelles of the sol takes place. As a result, a plastic mass with varied amounts of homogeneous swollen gel is obtained. At the same time the sol, by losing its solvent, forms a gel, that is, becomes gelated. In the production of uniform plastic masses, therefore, the use of low temperatures, higher pressures and longer application of pressure are important.

F-4. L.I. Sacharov. Trans. Kirov. Inst. Chem. Tech. Kazan No. 4-5, 167 (1935)

Solvents in the Manufacture of Smokeless Powder

The paper describes the application of ether-alcohol in the manufacture of smokeless nitrocellulose powders and gives a complete example covering all stages of manufacture and showing the calculation of the ether-alcohol balance.

F-10. J. Grevy. Comptes Rendus 200, 742-4 (1935)

The Viscosity of Very Dilute Solutions of Nitrocellulose in Ether-Alcohol

Grevy studied the effect of concentration of nitrocellulose on viscosity when dissolved in ether-alcohol. He found that while solutions of high concentration show a minimum viscosity at a composition of 35 parts of ethyl alcohol and 65 parts of ether, the specific viscosity of solutions of very low concentration does not depend upon the composition of the solution of the solvent. The lowering of viscosity with age varies and reaches a maximum value with a solvent that contains 60 per cent alcohol.

F-11a T.Tomonari. Cellulosechemie 16,49-56(1935)

Solubility and Viscosity of Nitrocellulose

Tomonari finds that the Staudinger rule does not apply in the case of nitrocellulose solutions studied by him. There is included theoretical discussion that may justify further study in anticipation of experimental work.

F-12. T.Nakashima and N.Saito. J.Soc.Chem.Ind.,Japan 38,
Suppl. 232-4 (1935)

The Heat of Solution and Swelling of Cellulose Derivatives

The following table is given for the heat of swelling and of solution in calories per gram:

	<u>Trinitrocellulose</u>	<u>Collodion</u>
Acetone	18.5 (clear sol'n)	21.2 (clear sol'n)
Ethanol	3.0	13.9
Methanol	6.0	16.6 (clear sol'n)
Benzol	2.4	8.6

A curve is also shown for the solubility and heat evolution in acetone benzene mixtures. It is shown that

$$Q = q_s - (q_g + q_d + q_t)$$

where Q = the experimentally measured heat evolution per gram.

q_s = heat of solvation

q_g = heat of tearing apart the lattice.

q_d = the work of dissociating the associated solvent molecules.

q_t = the work of separation of dissolved substances.

From the data it seems that as swelling proceeds a considerable increase in heat evolution takes place until the point where complete solution occurs, when a levelling off is seen. It is believed, therefore, that the heat of evolution would be at least a qualitative indication of the degree of swelling but the article is not too specific on this point.

F-13. M.Mathieu. Chim.Ind. 33,20-34 (1935)

Oils and Plastic Materials A Theory

Mathieu offers a theory to explain the plastic properties of certain materials. The change of mechanical properties of a nitrocellulose thread by swelling with acetone vapor is attributed to a change in crystal structure. Here again the original article should be given further study if experimental programs are laid out in this direction.

F-14. M.Mathieu. Compt.Rend. 200,401-3 (1935)

Structure of Trinitrocellulose

This study concerns the structure of trinitrocellulose. It is concluded that the molecular chains are folded, the folds repeating themselves at intervals of 5 glucose units. The NO₂ groups are probably arranged in regular intervals along the molecular chains.

F-15. Y.Y.C.Yen. Chemistry (China) 2,669 (1935)

Improving the Bulk Density of Smokeless Powder

Yen discusses a method of improving the bulk density of smokeless powders. This includes a procedure of adding alcohol only during the dehydration and not during the colloidizing of the nitrocellulose. "Stoving" is carried out at 45-50°C. for 10 hours. Smokeless powder which has normally a density of .805 had a density of .83 when this method was used (these densities appear low; it may be accounted for by the perforations of the grains in question).

F-16. J.Desmaroux and M.Mathieu. Mem.Poudres 26,180-203(1934-5)

The Action of Acetone on Nitrocellulose

Fibers of 11.6 per cent and 13.52 per cent nitrogen were exposed to acetone vapor of known pressure and the dependence of the acetone concentration of the threads on the pressure of the acetone vapor was determined and the results so found were compared with x-ray studies of swelling. The thermodynamic study of two nitrocelluloses of varying per cent nitrogen showed that the curves of molar acetone concentration-activity are almost straight lines (which is true only for solutions); irregularities are not observed. This was substantiated by x-ray diagrams of threads in equilibrium with acetone vapor of a definite pressure. The diagrams changed steadily with increasing acetone concentration of the threads without evidence for the formation of definite compounds. Acetone and nitrocellulose as long as no gelatinization has

yet occurred combine to form a solid solution. Diagrams indicate that nitrocellulose can take up acetone under limited enlargement of the spacing of the glucose chains in the direction of the plane of the ring. This spreading reaches its maximum value when one mol nitrocellulose takes up one mol acetone. At a definite acetone concentration collapse of the crystalline thread structure occurs with gelatinization. The gel gives a diagram which is characterized by the disappearance of every regular spacing of the glucose chain.

G-5. J.W.McBain, E.M.Grant, L.E.Smith. J.Phys.Chem. 38, 1217-31 (1934)

Viscosity of Guncotton in Various Solvents and Mixtures

McBain et al used 100 solvents and mixtures in the treatment of guncotton that was made by various manufacturers. Earlier results reported in 1926 were extended. Some of this work included experiments in which the solutions were held at 55°C. over long periods of time. Some of the solutions approached the viscosity of the pure solvent. In a few cases the viscosity curves went through a sharp minimum and later the solutions underwent gelling.

Nitrocellulose of 12.2 per cent nitrogen was studied. Drying of methyl alcohol diminishes its solvent power. The viscosity is a function of a large number of variables due to structure viscosity changes and not to fluctuations in chain length. The lower the relative viscosity, the better the solvent. A review of various ways of testing solvent power is given.

G-7. G.L.Wilson and F.D.Wiles. Phil.Trans., Roy Soc.(London) A, 233, 247-77 (1934)

The Solvation of Nitrocellulose in Acetone-Water Mixtures

A careful experimental study which may well be applicable for other work on solvation by mixtures. There are indications that some H₂O is needed to improve the solvent power of the acetone.

G-11. J.J.Trillat. J.Chim.Phys. 31, 125-37 (1934)

Nitrocellulose Films and Their Polymorphism

Trillat reports on X-ray study of a 12.95 per cent nitrogen product in acetone. Certain experiments were made in ethyl acetate also. The crystal structure as revealed by the X-ray study is greatly altered by the swelling action of acetone.

- G-12. A.Beck,L.Clement, and C.Riviere. Monit.Produits Chim.
16,73-4,3-7(1934)
Chemical and Physical Nature of Nitrocellulose

Beck et al state that cellulose may be nitrated to any desired nitrogen content and that such products are chemically homogeneous but physically heterogeneous.

- G-13. M.Demougin. Mem.Poudres 26,37-41 (1934-5)

Comparison of Nitrogen Content and
Solubility of Nitrocellulose

Smokeless powders were studied over a period of one year. He points out that in general the solubility of the nitrocellulose is a function of the nitrogen content except in certain cases where strong bleaching, an increase in nitrating temperature, increased stabilization, and prolonged beating increase the solubility. Short time nitrations cause a product to be more heterogeneous. The use of the Thomson displacement process tends to increase the solubility.

- G-18. M.Kostevich. Separate, Belgrade 1934, p. 12.

Use of X-Rays in Smokeless Powder
Manufacture, etc.

Kostevich states that X-ray tests should be used only for an approximate evaluation in the control of manufacture of smokeless powders. Photomicrography with the aid of cinematographic apparatus is useful for a determination of the colloidal state and the degelatinization of the powder.

- G-20. I.Sakurada and M.Shojino. Koll.Z. 68,300-5(1934)
J.Soc.Chem.Ind.,Japan 37,
Suppl., 603(1934)

Relation Between Solvent Power of Organic Liquids and
the Viscosity of Cellulose Ester Solutions

The solubility power of solvents for cellulose esters, due to the complex character of the material, cannot be inferred from the concentration in the saturated state without further study. The determination of the solubility power from the comparison of the viscosity of solutions of equal concentration has theoretical and practical difficulties. It is proposed to dilute the solutions to be tested with a neutral fluid and then to determine the solubilizing power of the pure material from that of the diluted solvent. This was done for 11 solutions in connection with nitrocelluloses of 13.7 and

11.6 per cent nitrogen. The measurement of the viscosity shows that for low nitrated nitrocellulose the best solvents (as determined by the proposed method) are solutions with the smallest specific viscosity. For high nitrated cellulose the relation is not so simple. The better the solvent the smaller is the specific volume of the low nitrated nitrocellulose; that of the higher nitrated cellulose is almost constant. The particles are without charge and almost spherical.

G-24. I. Sakurada and K. Futino. Sci. Papers Inst. Phys. Chem. Res.
(Tokyo) 24, 193-210 (1934)

Ring Fiber Structure and Orientation of
Micelles in Films as Shown by X-Rays

This study concerns orientation of micelle groups in nitrocellulose films. Pressed films of trinitrocellulose as well as unstretched films show ring fibering with the fiber axis normal to the film.

G-26. L. Medard. Mem. Poudres, 26, 69-85 (1934-5)

Measurements of the Gelatinizing of Nitrocellulose
by Four Binary Mixtures of the Type Alcohol-Ether

Medard makes measurements of the gelatinizing of nitrocellulose by binary mixtures of the basic type alcohol plus ether. A series of ether-like substances which alone have no gelatinizing action on nitrocellulose, together with alcohol which shows a strong gelatinizing power, were studied systematically. The secondary components included dioxane, cineol, methyl furan, methylal, and ethyl ether. The greatest gelatinizing power was found with a mixture of 35 parts of alcohol and 65 parts of ether; also with equal parts of alcohol and dioxane. The examination shows no basis for believing that the maximum gelatinizing power of these mixtures is related to a simple stoichiometric relation of the components.

H-1. J.W. McBain, S.J. Good, A.M. Bakr, Trans. Far. Soc. 19, 1086-
D.P. Davies, H.J. Willavoy, and 1100 (1933)
R. Buckingham

Sorption of Vapors by Nitrocellulose

McBain et al study the sorption of vapors by nitrocellulose. Nitrocellulose was exposed to several vapors and the amount taken up by the nitrocellulose was determined. The adsorption varies 100-fold between best solvents and those that are least effective. The difference in the quantity taken out is ascribed to a change in the structure of the nitrocellulose which only the better solvents can produce. There is no saturation value and the quantities of vapor do not depend upon their molecular weight since there are no fixed outer surfaces and no definite number of binding points. The article deserves further attention, particularly in connection with any projected experimental program.

H-2. S. Yamamoto. Cellulose Ind. (Tokyo) 19, 4-9 (1933)

The Fractionation of Nitrocotton
Solution of Nitrocotton in Acetone-Water

This relates to fractionation of nitrocotton by means of acetone-water mixtures. Nitrates examined ranged from 10.4 to 13.36 per cent nitrogen. It was found that the solution of nitrocotton in an acetone-water mixture depends upon its nitrogen content. The upper part of the solubility curve of nitrocotton plotted against varying content of acetone in the acetone-water mixture shows a steep inclination to the axis while the lower part inclines more gently. The former part corresponds to precipitation of nitrocotton in larger agglomerates rich in nitrogen and the latter to the precipitation of nitrocotton in lower degree of agglomeration. The nitrocotton precipitated in this part consists of various disintegrated products of the original nitrocotton.

H-3. M. Mathieu. Trans. Far. Soc. 29, 122-32 (1933)

Structural Changes in Nitrocellulose

Mathieu studies structural changes in nitrocellulose. X-rays of nitrated cotton with 11 to 13.9 per cent nitrogen all show a sharp ring corresponding to a well defined lattice constant which increases regularly with increasing total content.

H-4. P. Demougin. Compt. Rend. 196, 408-10 (1933)

The Solubility of Guncotton

High nitrated cotton (CP₁) is partially soluble in ether-alcohol, the insoluble fraction swelling only. Repeated fractionations can improve the solubility. Solubility is also increased as beating becomes more effective. It is assumed that only the surface part of the nitrocellulose particle goes into solution. The remaining insoluble nitrocellulose acts as a semi-permeable membrane and prevents the soluble nitrocellulose on the inside from dissolving. The osmotic pressure causes swelling. This can explain the dependence of the directly determined solubility of guncotton on the nitrogen content. With decreasing per cent nitrogen, the solubility increases regularly until from a definite per cent nitrogen on, the solubility becomes much greater. This means the osmotic pressure has become so large that the resistance of the membrane is overcome and the soluble material on the inside can dissolve.

H-13. K. Atsuki and M. Ishiwara. J. Soc. Chem. Ind., Japan (Suppl.) 36, 540-44 (1933)

The Structure of Cellulose Gels VII X-Ray Study of Cellulose Nitrate Gel

Cellulose is nitrated at various temperatures. The viscosity, the mechanical properties of the acetone film and the structure of acetone or alcohol-ether films were studied by X-rays. At the same time a nitrocellulose (13 per cent nitrogen) -nitroglycerine gel was studied by X-rays. The structure of films of nitrocellulose with 11.2-11.4 per cent nitrogen is almost amorphous. The acetone film has a more uniform structure without inner distortion, while the alcohol-ether film consists of a network structure with inner distortion and heterogeneous distribution of the molecular surface contact.

On drying an acetone solution of cellulose nitrate, the solute may be kept in a state of dispersion until the amount of acetone becomes very little, and this now adheres to the cellulose nitrate as a molecular compound. In an ether-alcohol solution, however, ether evaporates more quickly than alcohol and the solute becomes insoluble, remaining in a swollen state during drying. Hence the film from acetone solution is uniform.

H-16. A. Stettbacher. Leipzig (1933) Book

Die Schiess und Sprengstoffe

Stettbacher mentions that the most dense and moisture

insensitive powder comes from acetone gels since acetone also dissolves the high nitrated cotton while ether-alcohol causes a swelling only. Guncotton is insoluble in cold or hot water but easily soluble in acetone, ethyl acetate, nitro benzene, and pyridine. The most favorable volume relation is one volume ether (0.720) and one volume alcohol (99½ per cent). With 95 per cent alcohol maximum solubility occurs with 2 volumes ether to one volume alcohol. At low temperatures high nitrated cellulose is gelatinizable and soluble in ether-alcohol.

H-17. F.D.Miles. Trans.Far.Soc. 29,110 (1933)

Molecular Aggregation of Nitrocellulose

Miles offers data to support the general hypothesis that all chain molecules are nitrated to approximately the same extent so that the chance of any one being completely nitrated to trinitrate before the rest undergo the same nitration is very small.

J-1. Y.Nisizawa. Koll.Z. 56,179-94 (1931)

Structure Viscosity Measurements of Cellulose Derivatives in Organic Solvents and the Influence of Additions on the Viscosity

Nisizawa discusses the influence of adding various organic and inorganic agents to a nitrocellulose ether-alcohol colloid. Some work was also done with acetone as a colloidizing agent. Some of the substances used raise the viscosity of the mass; others lower the viscosity.

J-2. J.Desmaroux. Mem.Poudres (2),24,101-5 (1931)

Distribution of Solvent in the Web of Powder Grains

Desmaroux discusses the distribution of solvent in a powder grain. He states that there is a regular increase in solvent content from the surface to the center during solvent recovery but that for dried powders the solvent distribution was uniform.

J-3. A.J.Drinberg. J.Appl.Chem.(USSR)1,(4),87-116(1931)

Solvation and Viscosity of Nitro and Acetyl Cellulose Solutions

Drinberg discusses the effect of concentration, depolymerization, dispersion medium, and temperature on the viscosity and the solvation of nitrocellulose and of acetyl cellulose solutions. Conclusions are as follows:

(a) The specific degree of solvation decreases with increased concentration but the total volume taken up by the solvated phase increases, and the more so the less the ester is depolymerized.

(b) The length of molecular chains decreases with the depolymerization of the cellulose ester.

(c) With decreasing molecular volume of the peptizer, the viscosity and the degree of solvation of the solution increase. Alcohol sols show the minimum of viscosity and degree of solvation at a higher alcohol concentration, the higher the molecular weight of the peptizer.

(d) With increased temperature the viscosity and the degree of solvation in sols with a peptizer and in sols with a smaller ratio of coagulator to peptizer the peptization number decreases. However, in sols in which this ratio between coagulation and peptization number exists, on raising the temperature coagulation occurs which can be called a kinetic phenomenon tied up with a disturbance of the sol structure on temperature rise.

J-4. J.Desmaroux. J.Chim.Phys. 28,163-73 (1931)

Affinity of Nitrocellulose for Gelatinizing Agents

A discussion of the oxonium theory of gelatinization is presented including some experimental work on 11.8 per cent nitrogen.

K-1. Blanchard. Mem.Poudres 24,241-4 (1930-1)

Graining

Blanchard discusses the mathematical relationship between length of die, graining pressure, viscosity of nitrocellulose, and the appearance of the finished powder.

K-2. J.Desmaroux. Mem.Poudres 24,101,265-81 (1930-1)

Distribution of Residual Solvent in Nitrocellulose Grains

Desmaroux discusses the matter of solvent distribution in the smokeless powder grains.

K-3. J.J.Trillat. J.Phys.Rad.(7),1,340-350 (1930)

Study of the Constitution of Nitro
and Acetyl Cellulose

Trillat found that above 12 per cent nitrogen the tri-nitrocellulose diagram predominates in a crystalline and an amorphous phase. Films show essentially the same structures as fibers but interferences are less sharp. The amorphous diagrams show less difference.

K-4. W.J.Jenkins,H.B.Bennett, J.Phys.Chem.34,2318-29,2330-42
L.Rubinstein. (1930)

Sorption Experiments with Nitrocellulose
Sorption of Vapors on Nitrocellulose

Jenkins et al present two papers both of which deal with sorption experiments in which nitrocellulose is exposed to various vapors.

K-8. J.Desmaroux. Mem.Poudres 24,265-81 (1930-31)

Partial Pressure of Ether and Alcohol
in Gelatinized Nitrocellulose

Nitrocellulose has no preferential absorption for ether, alcohol, or mixtures thereof. Small amounts of ether are held more tenaciously than small amounts of alcohol, however.

L-1. A.J.Phillips. J.Phys.Chem. 33,118-30 (1929)

The Behavior of Nitrocellulose Gels
in Polarized Light

Phillips discusses the behavior of nitrocellulose gels in polarized light. This paper has importance in connection with any microscopic work that deals with the examination of partially colloided nitrocellulose.

L-2. A.Michel-Levy and H.Muraour. Compt.Rend.189,1192-4(1929)

The Microscopic Examination of Colloidal
Nitrocellulose in Polarized Light

Michel et al discuss the microscopic examination of colloided nitrocellulose in polarized light. The studies include

work with a product that has 11.7 per cent nitrogen; also one comprising two components that contain respectively 11 per cent and 13 per cent nitrogen and have the same overall nitrogen content. The highly nitrated fibers could be detected in the colloids. The presence of fibers of highly nitrated cellulose coincided with an increased rate of combustion of powders containing them owing to the formation of surface cavities by the rapid combustion of the highly nitrated portions and the consequent increase in emission surface.

L-7. E.W.Mardles. Koll.Z. 49,4-11,11-16 (1929)

Solubility of Cellulose Derivatives

An extensive discussion is given of the relations between solubility power, viscosity, degree of dispersion, etc. for pure solvents and mixtures. The paper should be read further.

M-1. W.Kumichel. Kolloidchem.Beihette 26,161-98 (1928)

Fractional Precipitation and Ultra Filtration of Nitrocellulose

Kumichel has done work in which cellulose nitrate is fractionated into two components, A and B. B is made up of degradation products of nitrocellulose; A exhibits the reactions of very pure nitrocellulose. Per cent nitrogen is the same in both components. Viscosity of A is very much greater than viscosity of B. Solubility of A and B in ether alcohol remains the same. For all technical applications A is better than the original mixture; B is unsuitable for explosives manufacture. (It is probable that some emphasis is placed on the instability of the degraded nitrocellulose product.)

M-2. F.Olsen. Coll.Symp.Mon. 6,253 (1928)

Influence of Gel Structure Upon the Technology of Smokeless Powder Manufacture

Fred Olsen discusses the influence of gel structure upon the technology of smokeless powder manufacture. He discusses both cotton and wood pulp. He mentions the effect that beating has on the structure indicating improved gelatinization with beating of base fiber. He discusses lack of uniformity of nitration. In regard to the action of solvents he states that there is a prior swelling by the vapor. This is followed by a dispersion of the nitrocellulose. Pictures are shown to illustrate the swelling. The effect of extrusion, mixing, etc. on the homogenization of the gel is also illustrated.

O-1. J.Desmaroux. Mem.Poudres 22,259-84 (1926)

Microscopic Studies of the Structure
of Poudre B

Desmaroux describes microscopic studies of the structure of Poudre B. Guncottons which have a solubility as high as 25 per cent in ether-alcohol are a physical mixture of soluble and insoluble fibers. Some of the insoluble fibers are superficially etched and corroded by the solvent. He describes a technique for examining these residues under the microscope.

O-4. A.Highfield. Trans.Far.Soc. 22,57-75 (1926)

Colloidal Properties of Nitrocellulose
in Solvent Mixtures

Polar solvents and non-polar solvents are inferior in solvent power to mixtures. U-curves, showing viscosity maxima were found in ether-alcohol-H₂O, acetone-alcohol-H₂O, nitrobenzene-alcohol, aniline-alcohol-nitrobenzene, nitro-aniline-alcohol, ether-methyl alcohol-H₂O, propyl alcohol-ether, butyl alcohol-ether, acetone-benzene, acetone-ether-H₂O (on 12.2 per cent nitrogen nitrocellulose). Progressively decreasing nitrogen content increases the range of solvent mixtures down to 10.5 per cent, below which solubility diminishes, as is also the case with very highly nitrated cottons. The best solvent mixture contains polar and non-polar groups balanced in optimum proportions.

The solvent which gives the sol of minimum viscosity is not necessarily the best solvent from the point of view of ease of solution, due to the fact that the viscosities of the two components of the solvent mixtures are unequal. Hence, the optimum solvent contains more of the ingredient of higher viscosity than does the solvent which gives the sol of minimum viscosity. Qualitative criteria from viscosities are satisfactory.

O-5. J.W.McBain,C.E.Harvey, J.Phys.Chem. 30,312-52(1926)
and L.E.Smith.

Apparent Viscosity of Solutions of
Guncotton in Various Solvents

The effect of variables on viscosity:

1. Concentration: no good formula available.
2. Temperature: Temp. coefficient is large.
3. Pretreatment of nitrocellulose.

4. Temperature of preparation of solution: the higher the temperature, the lower the viscosity, which persists even after storage for several months.
5. Type of solvent: mixtures best. Best solvents give least viscous solutions.
6. Age and degradation.

A detailed critical literature review is also given.

R-1. A.Szegvari. Koll.Z. 34,34-37 (1924)

Gelatinization of Nitrocellulose Solutions

Nitrocellulose solutions in solvents like amyl acetate may be diluted with liquids in which they are not alone soluble, such as benzine. Such mixtures then gelatinize if the temperature is raised beyond a certain point, becoming liquid on cooling.

S-2. E.W.J.Mardles. J.Soc.Chem.Ind.42,T,127-36,207-11(1923)

Study of Solvents for Various Cellulose Esters. The Correlation of Solvent Power and the Viscosity of Cellulose Ester Solutions

A number of binary and ternary mixtures were studied, including effects on cellulose nitrate. There appears to be no correlation between the physical and chemical constants of the various grades with their solubility. It often happens, in a mixture, that the optimum solvent mixture occurs at simple molecular proportions, probably due to the molecular nature of the swelling.

U-1. H.Marqueyrol and Florentin. Mem.Poudres 19,150-67(1921)

Gelatinization of Nitrocellulose

Marqueyrol discusses gelatinizers and their most important properties. A list is given of gelatinizer patents since 1900. The gelatinization of certain nitrocottons by alcoholic solutions of various types of gelatinizers including substituted ureas, esters, and cyclic ketones is described.

U-2. R. Robertson. Koll. Z. 28, 219-23 (1921)

Nitrocellulose

Robertson gives a review of some of the well known phenomena that attend the manufacture of smokeless powder. He includes a statement that at a definite relation of alcohol to ether a minimum in the viscosity of a collodion solution occurs independent of the nitrocellulose content. Solutions in acetone and water are similar.

P-1. U.S. Patent 1,752,881

This is an American Patent taken out by Borland and the American Powder Company. It claims a process for the hardening of grains of nitrocellulose for smokeless powders by introducing the liquid solvent as a fine spray.

P-2. U.S. Patent 1,713,505

This is an American Patent taken out by Hawkesworth. It describes a simultaneous drying, dissolving and stabilization of nitrocellulose by means of mono nitro toluene.

P-8. British Patent 324,044 (1930)

This was taken out by the Imperial Chemical Company and O.W. Stickland. The process employs a nitrocellulose that is wholly or mainly of the insoluble variety with a nitrogen content of 13.2 per cent or more, preferably about 13.45 per cent.

P-9. British Patent 353,634 (1929)

This was taken out by Wolff and Company. It describes the use of low temperatures (below 0°C. (?)) in conjunction with methyl or ethyl alcohol for preparing propellant powders from nitrocelluloses which would not gelatinize in the solvent at ordinary temperatures. The nitrocellulose in question contains more than 12.8 per cent nitrogen. Reduction in temperature is also advantageous for mixtures of solvent that contain ether and alcohol.

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ABSTRACT:

Nitrocellulose to Smokeless Powder

This report is concerned with the colloidizing step by which nitrocellulose is prepared for extrusion into powder grains. The powder grains of wood cellulose origin have a somewhat more brittle nature than in the case of cotton products. Polarized light and X-ray examination reveal that the powder grains as now produced are for the most part heterogeneous in composition. When the "green" powder is freed of solvent the total shrinkage is related to total solvent used in the colloidizing, while the resulting distortion of shape is related to the manner in which the solvent leaves the grains. No serious evidence has been found that shows that low viscosity nitrated products are wholly unsuitable for use.

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